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Standard Test Methods for Resistance of Glass Containers to Chemical Attack¹

This standard is issued under the fixed designation C 225; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the evaluation of the resistance of glass containers to chemical attack. Three test methods are presented, as follows:

1.1.1 *Test Method B-A* covers autoclave tests at 121°C on bottles partially filled with dilute acid as the attacking medium.

1.1.2 *Test Method B-W* covers autoclave tests at 121°C on bottles partially filled with distilled water as the attacking medium.

1.1.3 *Test Method P-W* covers autoclave tests at 121°C on powdered samples with pure water as the attacking medium.

1.2 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

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:

A 569/A 569M Specification for Steel, Carbon (0.15 Maximum Percent), Hot-Rolled Sheet and Strip Commercial Quality²

D 1125 Test Methods for Electrical Conductivity and Resistivity of Water³

D 1193 Specification for Reagent Water³

E 11 Specification for Wire-Cloth Sieves for Testing Purposes⁴

¹ These test methods are under the jurisdiction of ASTM Committee C-14 on Glass and Glass Products and are the direct responsibility of Subcommittee C14.03 on Chemical Properties.

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² *Annual Book of ASTM Standards*, Vol 01.03.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁴

3. Significance and Use

3.1 The solubility of glass in contact with food, beverages, or pharmaceutical products is an important consideration for the safe packaging and storage of such materials. Autoclave conditions are specified since sterilization is often employed for the packaging of the product. It also represents one of the most extreme conditions, particularly of temperature, that containers will ordinarily experience. Any of the three test methods described may be used to establish specifications for conformity to standard values, either as specified by a customer, an agency, or “The United States Pharmacopeia:”

3.1.1 *Test Method B-A* is intended particularly for testing glass containers primarily destined for containment of products with a pH under 5.

3.1.2 *Test Method B-W* is intended particularly for testing glass containers to be used for products with a pH of 5.0 or over.

3.1.3 *Test Method P-W* is a hydrolytic autoclave test primarily intended for evaluating samples from untreated glass containers. It is often useful for testing the resistance of containers of too small capacity to permit measurements of solubility on the unbroken article by the B-W test method. Yielding the water resistance of the bulk glass, it can also be used in conjunction with the B-W test method to distinguish whether the internal surface of a container has been treated to improve its durability.

3.2 All three test methods are suitable for specification acceptance.

4. Purity of Reagents

4.1 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.⁵ 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.

4.2 Unless otherwise indicated, references to water shall be understood to mean distilled water or other water meeting the requirements for one of the types of reagent water covered by Specification D 1193.

TEST METHOD B-A—RESISTANCE OF BOTTLES TO ATTACK BY DILUTE ACID

5. Apparatus

5.1 *Autoclave or Steam Sterilizer*, capable of withstanding a pressure of 165 kPa (24 psi) and, preferably, equipped with a constant-pressure regulator or other means for maintaining the temperature at $121 \pm 0.5^\circ\text{C}$ ($250 \pm 0.9^\circ\text{F}$). This temperature shall be checked by means of a suitably calibrated instrument. The autoclave shall be capable of accommodating at least six and preferably twelve of the largest containers to be tested. It shall be equipped with a rack for supporting the samples, a thermometer, a pressure gage, and a vent cock.

6. Reagents and Materials

6.1 *Acetone*, USP grade.

6.2 *Methyl Red Indicator Solution*—Dissolve 24 mg of the sodium salt of methyl red in 100 mL of water. If necessary, neutralize the indicator solution with 0.020*N* sodium hydroxide (NaOH) solution so that the titer of five drops of the indicator solution in 100 mL of the special distilled water does not exceed 0.02 mL of 0.020*N* NaOH solution. In titrations using the methyl red indicator solution, the end point shall be taken at a pH of 5.6.

6.3 *Phenolphthalein Indicator Solution*—Dissolve 0.5 g of phenolphthalein in 60 mL of ethyl alcohol (95 %) and dilute with water to 100 mL.

6.4 *Sodium Hydroxide Solution, Standard (0.020*N*)*—Dissolve 100 g of NaOH in 100 mL of water in a 150-mL test tube. Avoid wetting the top of the test tube. Stopper the tube loosely with a stopper covered with tinfoil and allow to stand in a vertical position until the supernatant liquid is clear. Withdraw some of the clear solution in a measuring pipet and deliver 1.3 mL into a paraffin-lined bottle containing 1 L of carbon dioxide (CO₂)-free water. Stopper the bottle with a two-hole stopper carrying a glass siphon tube (for delivering the solution to a buret) and a soda-lime or soda-asbestos guard tube. Standardize the 0.020*N* NaOH solution against the National Institute of Standards and Technology Standard Sample No. 84h of acid potassium phthalate. Transfer 0.2000 g of the phthalate to a 250-mL Erlenmeyer flask and dissolve in about 75 mL of CO₂-free water. Add five drops of phenolphthalein indicator solution and titrate with the NaOH solution

to the first persistent pink color. Adjust the standard NaOH solution to 0.020*N* strength.

6.4.1 Calculate the normality *N* of the NaOH solution as follows:

$$N = 0.9798/\text{mL of NaOH} \quad (1)$$

6.5 *High-Purity Water*—This water shall be free of heavy metals, particularly copper, as shown by a dithizone test⁶ and have a conductivity (consult Test Methods D 1125) not exceeding 0.15 $\mu\text{S/cm}$.

6.5.1 The source water shall be distilled, then passed through a deionizer cartridge packed with a mixed bed of nuclear-grade resin,⁷ then through a cellulose ester membrane having openings not exceeding 0.45 μm .⁸ Pass the purified water through an in-line conductivity cell to verify its purity. After flushing discharge lines, suitable water should be dispensed directly into the test vessels.

NOTE 1—Copper tubing should not be used in the discharge lines. TFE-fluorocarbon or pure tin are suitable.

NOTE 2—Reference should be made to Specification D 1193. Type I reagent water as defined therein complies with the present 6.5. In the interest of practicality and demonstrated sufficiency, 6.5 allows the following deviations from Type I reagent water specifications.

(1) Source water is unspecified whereas Type I specifies source water having a maximum conductivity of 20 $\mu\text{S/cm}$ at 25°C.

(2) The final step is filtration through a membrane having openings not exceeding 0.45 μm . Type I directs filtration through a 0.2- μm membrane.

(3) The conductivity immediately before dispensing is required not to exceed 0.15 $\mu\text{S/cm}$ at 25°C whereas Type I is limited to 0.06 $\mu\text{S/cm}$ at 25°C.

The distillation step is essential to minimize or avoid cultivation of microorganisms in the ion-exchange bed and consequent clogging of the membrane filter. When preceded by distillation, the ion-exchange bed should have a long life, but as the conductivity begins to rise toward the limit it should be replaced by a new bed.

Distillation from phosphoric acid with a conductivity of the product between 0.5 and 1.0 $\mu\text{S/cm}$ was specified as water for extraction in Test Methods C 225. Water prepared as described herein gave results averaging about 8 % higher than water prepared by distillation from phosphoric acid when Test Method B-W was applied to soda-lime and borosilicate glass bottles in seven laboratories. The trend to slightly greater extraction may be associated with the higher average purity of this water. The limit on conductivity of 0.15 $\mu\text{S/cm}$ for water prepared by this means was set because water of less conductivity is readily obtained and when 0.15 $\mu\text{S/cm}$ is exceeded, the conductivity rises rapidly on further use of the system.

6.6 *Sulfuric Acid, Standard (0.020*N*)* containing approximately 0.58 mL of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) in 1 L of solution. Prepare 0.1*N* H₂SO₄ containing 3.0

⁶ Feigl, Fritz, "Spot Tests in Inorganic Analysis," D. Van Nostrand Co., Inc., Princeton, NJ, 1958, p. 90; H. J. Wichman, "Isolation and Determination of Traces of Metals," *Industrial and Engineering Chemistry*, Vol 11, No. 2, 1939, pp. 67–72.

⁷ A nuclear-grade resin mixture of the strong acid cation exchanger in the hydrogen form and the strong base anion exchanger in the hydroxide form with a one-to-one cation to anion equivalence ratio, such as that available from the Millipore Corp., 80 Ashby Rd., Bedford, MA 01730; Barnstead Co., 225 Rivermoor St., Boston, MA 02131; Illinois Water Treatment Co., 854 Cedar St., Rockford, IL 61105; or Vaponics, Inc., 200 Cordage Park, Plymouth, MA 02360, has been found satisfactory for this purpose.

⁸ An in-line filter such as those made by the Millipore Corp., Gelman Instrument Co., 600 S. Wagner Rd., Ann Arbor, MI 48106; and Schleicher and Schuell, Inc., 540 Washington St., Keene, NH 10003 has been found satisfactory for this purpose.

⁵ *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.

mL of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84)/L. Dilute 200 mL of the 0.1N H_2SO_4 to 1 L and standardize against 0.020N NaOH solution, using methyl red indicator solution. Finally, adjust the standard H_2SO_4 to 0.020N strength.

6.7 *Sulfuric Acid, Standard (0.0005N)*—Mix 1 volume of 0.1N H_2SO_4 with 199 volumes of water. Adjust the strength to be $0.0005 \pm 0.000025N$.

6.8 *Sulfuric Acid, Standard (0.0002N)*—Mix 1 volume of 0.1N H_2SO_4 with 499 volumes of water. Adjust the strength to be $0.0002 \pm 0.00001N$.

7. Preparation of Sample

7.1 If the bottles are 168-cm³ (6-oz) capacity or over, select three bottles. If the bottles are smaller than 6-oz capacity, select a sufficient number so the contents can be combined to form three sets to give 100 mL/set. Rinse each container with two portions of the high-purity water, follow with two similar rinsings using acetone and dry with a stream of clean dry air.

8. Procedure

8.1 Fill the containers, at room temperature, to 90 % of overflow capacity with the attacking medium.

NOTE 3—If the bottles to be tested will neutralize more than the equivalent of 0.80 mL of 0.020N H_2SO_4 , use 0.0005N H_2SO_4 as the attacking medium. Otherwise, use 0.0002N H_2SO_4 as the attacking medium.

8.2 Cover each container individually with a chemical-resistant glass⁹ beaker or cap that has been digested with water for at least 24 h at 90°C (194°F) or 1 h at 121°C (250°F). These covers shall be of such size that the bottoms of the beakers or caps fit snugly down on the top rims of the containers. Place the containers on the rack in the autoclave. The sample rack must support the samples above water level. Close the cover securely, leaving the vent cock open. Heat until steam issues vigorously from the vent. Allow steam to issue from the vent for 10 min; then close the vent cock and increase the temperature at the rate of 1°C/min to 121°C taking 19 to 23 min. Maintain the temperature at $121 \pm 0.5^\circ\text{C}$ ($250 \pm 0.9^\circ\text{F}$) for 1 h, counting from the time when the holding temperature is reached. At the end of the hour, cool at the rate of 0.5°C/min to atmospheric pressure, venting to prevent formation of a vacuum. The time to cool from 121°C to atmospheric pressure should be from 38 to 46 min. Open the autoclave and remove the containers.

8.3 *Titration of Bottle Extract*—Cool the containers and contents to room temperature. With a pipet, transfer 100-mL portions of the test solution from the containers to 250-mL flasks of chemical-resistant glass.⁹ Add five drops of methyl red indicator solution to each flask and titrate with 0.20N NaOH solution.

NOTE 4—When titrations are under 1 mL, a microburet should be used.

⁹ Corning Pyrex-brand, manufactured by Corning Inc., Corning, NY 14831, Kimble Kimax-brand, manufactured by Kimble Glass, Inc., Crystal Ave., Vineland, NJ 08360, and similarly resistant borosilicate glass have been found satisfactory for this purpose.

9. Calculation and Report

9.1 Report the results as millilitres of 0.020N acid consumed in the test, A. Calculate as follows:

$$A = V - 0.98B \quad (2)$$

where:

V = 0.020N NaOH solution equivalent to 100 mL of the attacking medium, mL;

B = 0.020N NaOH solution used in the titration of 100 mL of bottle extract, mL; and

0.98 = factor applied to the titration of the bottle extract to correct that titration for loss of attacking medium during cooling of the autoclave.

TEST METHOD B-W—RESISTANCE OF BOTTLES TO ATTACK BY WATER

10. Apparatus

10.1 See Section 5.

11. Reagents

11.1 See 6.2-6.6.

12. Preparation of Sample

12.1 If the bottles are 168-cm³ (6-oz) capacity or over, select three bottles. If the bottles are smaller than 168-cm³ capacity, select a sufficient number so that the contents can be combined to form three sets to give 100 mL/set. Rinse each container with two portions of the high-purity water as described in 6.5.

13. Procedure

13.1 Fill the containers, at room temperature, to 90 % of overflow capacity with the high-purity water. Continue as described in 8.2.

13.2 *Titration of Bottle Extract*—Using a graduated cylinder, transfer 100-mL portions of the test solution from the containers to 250-mL flasks of chemical-resistant glass.⁹ Add five drops of methyl red indicator solution to each flask and titrate with 0.020N H_2SO_4 (Note 4). The time elapsing between opening the autoclave and titrating the solution should not exceed 1 h.

13.3 *Blank*—Titrate 100 mL of the high-purity water at the same temperature and using the same amount of indicator as in titration of the bottle extract in accordance with 13.2.

14. Calculation and Report

14.1 Report the results as millilitres of 0.020N H_2SO_4 required for titration of the sample, minus millilitres required for titration of the blank.

TEST METHOD P-W—RESISTANCE OF POWDERED SAMPLE TO ATTACK BY WATER

15. Apparatus

15.1 *Autoclave*—See 5.1.

15.2 *Flasks*—Erlenmeyer flasks of 250-mL capacity, made of chemical-resistant glass⁹ and suitably aged by previous treatment similar to the test or by previous use.