Designation: D4608 − 89 (Reapproved 2017)

Standard Test Method for Citrate in Detergents[1]

This standard is issued under the fixed designation D4608; 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 a potentiometric titration procedure for the determination of citrate in liquid and powder detergents.

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.* Material Safety Data Sheets are available for reagents and materials. Review them for hazards prior to usage. Specific safety precautions are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E70 Test Method for pH of Aqueous Solutions With the Glass Electrode

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

3. Summary of Test Method

3.1 The sample is titrated in an aqueous solution buffered at pH 8.5, with standard copper sulfate solution. The endpoint is detected potentiometrically using a copper ion selective electrode. The citrate content is calculated from the amount of standard copper sulfate solution consumed.

4. Significance and Use

4.1 This test method is suitable in research, development, and manufacturing control to monitor the level of citrate, a sequestering agent, in powder and liquid detergents.

4.2 Accurate determination of sequestering agent is important in evaluating cost and performance of detergent products.

5. Interferences

5.1 Other complexing agents such as nitrilotriacetic acid (NTA), ethylenedinitrilotetraacetic acid (EDTA), phosphates, etc. will titrate as citrate in this method. For accurate citrate determinations, such complexing agents must be absent.

6. Apparatus

6.1 *pH Meter,* with millivolt capability.[4]

6.2 *Copper Ion Selective Electrode.*[5]

6.3 *Calomel Reference Electrode.*[6]

6.4 *Glass Electrode Triple Purpose.*[7]

6.5 *Buret,* semi-micro, 25 mL capacity with 0.1 mL graduations.

6.6 *Magnetic Stirrer,* and TFE-fluorocarbon-coated magnetic stirring bars.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided it is first ascertained that the reagent is of

---

[1] This test method is under the jurisdiction of ASTM Committee D12 on Soaps and Other Detergents and is the direct responsibility of Subcommittee D12.12 on Analysis and Specifications of Soaps, Synthetics, Detergents and their Components.

Current edition approved Jan. 1, 2017. Published February 2017. Originally approved in 1986. Last previous edition approved in 2009 as D4608 – 89(2009). DOI: 10.1520/D4608-89R17.

[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] The last approved version of this historical standard is referenced on www.astm.org.

[4] An automatic titrator may be used.

[5] Orion Model 94-29A or equivalent has been found suitable for this purpose. Available from Orion Inc.

[6] Orion Model 90-22 or equivalent has been found suitable for this purpose. Available from Orion Inc.

[7] Corning Model No. 476022 or equivalent has been found suitable for this purpose. Available from Corning Inc.

[8] *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.

sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity.

7.3 *Hydrochloric Acid Solution (1 + 1)*—Slowly mix 1 volume of concentrated hydrochloric acid (sp gr 1.19) with 1 volume of water.

7.4 *Sodium Hydroxide Solution (20 %)*—Prepare a 20 % aqueous solution of sodium hydroxide.

7.5 *Sodium Hydroxide Solution* (0.1 *N*)—Prepare a 0.1 *N* aqueous solution of sodium hydroxide.

7.6 *Hydrochloric Acid Solution* (0.1 *N*)—Prepare a 0.1 *N* aqueous solution of hydrochloric acid.

7.7 *Borate Buffer Solution (pH 8.5)*—Dissolve 12.8 g of sodium borate ($Na_2B_4O_7{\cdot}10H_2O$) and 16.6 g of boric acid (H_3BO_3) in about 900 mL of water. Adjust pH to 8.5 with 20 % NaOH solution. Transfer quantitatively into a 1-L volumetric flask. Dilute to volume with water. Mix well.

7.8 *Sodium Thiosulfate Solution, Standard* (0.1 *N*)—Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3 5H_2O$) crystals in freshly boiled and cooled water and dilute to 1 L. Add 0.01 g of sodium carbonate and 0.5 mL of chloroform. Protect the solution at all times from direct sunlight. Standardize against potassium dichromate ($K_2Cr_2O_7$) by accurately weighing 0.221 g of finely powdered dry potassium dichromate and transferring solution to a 1-L iodine flask. Add 50 mL of water. Add 10 mL of concentrated hydrochloric acid and 3 g of iodate-free potassium iodide in 50 mL of water. Allow to stand in the dark for 5 min. Dilute to 400 mL with water and titrate immediately with the sodium thiosulfate using starch solution as indicator. Calculate the normality of the $Na_2S_2O_3$ solution as follows:

$$\text{Normality} = W/A \times 0.04902 \tag{1}$$

where:

W = weight of $K_2Cr_2O_7$,
A = mL of $Na_2S_2O_3$ solution required for titration of the $K_2Cr_2O_7$ solution, and
0.04902 = milliequivalent weight of $K_2Cr_2O_7$.

7.9 *Copper Sulfate Solution, Standard* (0.05 *M*)—Dissolve 12.48 g of copper sulfate ($CuSO_4{\cdot}5H_2O$) in 800 mL of water in a 1-L volumetric flask. Dilute to volume and mix well. Standardize against 0.1 *N* $Na_2S_2O_3$ (prepared in 7.8) by using a pipet, transferring a 25.0-mL aliquot of $CuSO_4$ solution into a 250-mL Erlenmeyer flask. Add 0.1 *N* NaOH solution dropwise until slightly turbid. Add 10 mL of acetic acid, 2 g of iodate-free potassium iodide and mix well. Titrate immediately with 0.1 *N* $Na_2S_2O_3$ standard solution using starch solution as indicator. Calculate the molarity of the $CuSO_4$ solution as follows:

$$\text{Molarity} = A \times N/25.0 \tag{2}$$

where:

A = mL of $Na_2S_2O_3$ solution required for titration of the $CuSO_4$ solution,
N = normality of $Na_2S_2O_3$ solution, and
25.0 = aliquot of $CuSO_4$ solution titrated.

7.10 *Citric Acid*—($C_6H_8O_7$).

8. Safety Precautions

8.1 All reagents and chemicals should be handled with care. Before using any chemical, read and follow all safety precautions and instructions on the manufacturer label. Clean up any spill immediately. For information on cleaning up spills refer to the *Laboratory Disposal Manual*, Manufacturing Chemists Association, Washington, DC.

9. Procedure

9.1 Accurately weigh (to the nearest 0.1 mg) enough sample to contain about 150 mg citrate as sodium citrate or 100 mg as citric acid. Quantitatively transfer to a 400-mL beaker with water and bring the volume to about 200 mL. While stirring with a magnetic stirrer, adjust the pH between 8 and 9 with dropwise additions of HCl (1 + 1) or NaOH (20 %). Add 25 mL borate buffer (pH 8.5). If necessary, carefully adjust the pH to 8.5 with NaOH (0.1 *N*) or HCl (0.1 *N*). Remove the glass electrode and insert the copper ion selective electrode.[9] Set the pH meter[4] on millivolt and begin to add copper sulfate solution in 1.0-mL increments. Near the end point add in 0.2-mL increments. Record the millivolt readings after each increment. Add at least five 0.2-mL increments past the end point. Calculate the end point by the second derivative method or by plotting millilitres of copper sulfate added versus millivolts. Calculate percent citrate as citric acid as follows:

$$\text{Citric Acid, \%} = A \times M \times 0.192 \times 100/W \tag{3}$$

where:

A = mL of $CuSO_4$ solution required for titration of sample solution,
M = molarity of $CuSO_4$ solution,
0.192 = milliequivalent weight of citric acid, and
W = g of sample taken.

10. Precision and Bias

10.1 The following criteria should be used to judge the acceptability of the results:[10,11]

10.1.1 *Repeatability (Single Analyst)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.06 weight % absolute at 12 df. Two such averages should be considered suspect (95 % confidence level) if they differ by more than 0.2 weight % absolute.

10.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.1 weight % absolute at 5 df. Two such averages should be

---

[9] The life of the copper ion selective electrode is finite. Its response needs to be occasionally checked by titrating an accurately weighed sample of citric acid.

[10] Supporting data are available from ASTM Headquarters, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Request RR:D12-1008.

[11] This statistical analysis was performed in accordance with Practice E180 for developing precision estimates.

considered suspect (95 % confidence level) if they differ by more than 0.4 % weight absolute.

10.1.3 *Checking Limits for Duplicates*—Report the percent of citric acid of the sample to the nearest 0.1. Duplicate runs that agree within 0.1 % absolute are acceptable for averaging (95 % confidence level).

10.1.4 The above precision data were derived from results of the cooperative tests by six laboratories on a powder detergent found to contain 3.5 % citric acid and a liquid detergent found to contain 7.7 % citric acid.

10.2 *Bias*—The exact level of citric acid in the powder detergent (10.1.4) was 3.4 %. The average percent citric acid found by the six participating laboratories, duplicate determinations on each of 2 days, was 3.5 indicating a high bias of 2.9 % relative. The exact level of citric acid in the liquid detergent (10.1.4) was not known.

11. Keywords

11.1 citrate content; copper ion selective electrode; sequestering agent

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/