

Test Method for Chelation Value of Polyaminopolycarboxylic Acids and Their Salts: Copper PAN

Developed in 1987 by AATCC Committee RR90; reaffirmed 1988 (with title change), 2002, 2012; editorially revised and reaffirmed 1989, 1997, 2007; revised 1992, 2018 (with title change); editorially revised 2010, 2019.

Foreword

This test method is an alternate to AATCC TM149, Test Method for Chelation Value of Aminopolycarboxylic Acids and Their Salts: Calcium Oxalate. Titration with a calcium salt using either oxalate or a dye indicator, as in AATCC TM149, yields a value that includes partially-substituted EDTA, HEDTA, DTPA, nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), glycolate and other weak chelating agents found in some commercial products. This alternative procedure excludes the effect of the partially-substituted products, providing a more stringent value.

1. Purpose and Scope

1.1 The active ingredient content of ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA) and their salts is usually expressed by the calcium chelation value (CaCV). This value indicates the amount of calcium (as calcium carbonate) which will be chelated by a known weight of chelating agent. This method excludes the effect of partially-substituted products.

2. Principle

2.1 Calcium chelation value is determined experimentally by titrating a weighed specimen of chelating agent with a copper nitrate solution of known concentration in the presence of PAN (1-(2-pyridylazo)-2-naphthol). Initially, the color of the solution is yellow-green due to free indicator. When all of the chelating agent has reacted with copper nitrate, the color of the solution changes to a permanent purple which is the end point.

2.2 The CaCV indicates the amount of calcium (as calcium carbonate) that will be sequestered by a known weight of chelating agent and is expressed as milligrams of calcium carbonate (CaCO_3) per gram of chelating agent (mg calcium carbonate/g chelating agent).

3. Terminology

3.1 **chelating agent**, *n.*—*in textile chemistry*, a chemical capable of deactivating metal ions by formation of a water-soluble complex. SYN: *sequestering agent*.

4. Safety Precautions

NOTE: These safety precautions are for information purposes only. The precautions are ancillary to the testing procedures and are not intended to be all inclusive. It is the user's responsibility to use safe and proper techniques in handling materials in this test method. Manufacturers MUST be consulted for specific details such as material safety data sheets and other manufacturer's recommendations. All OSHA standards and rules must also be consulted and followed.

4.1 Good laboratory practices should be followed. Wear safety glasses in all laboratory areas.

4.2 All chemicals should be handled with care.

4.3 In preparing, dispensing and handling glacial acetic acid and sodium hydroxide use chemical goggles or face shield, impervious gloves and an impervious apron. Concentrated acids and bases should be handled only in an adequately ventilated laboratory hood. CAUTION: Always add acid to water.

4.4 Cupric nitrate 2.5 hydrate is corrosive to the eye and skin and is harmful if inhaled. It is an oxidizing material and may react with organic materials. It should be handled only in an adequately ventilated hood.

4.5 Methanol is harmful if inhaled or swallowed and is a flammable liquid. It should be stored in the laboratory only in small containers away from heat, open flames and sparks. This chemical should not be used near an open flame and should be handled only in an adequately ventilated hood.

4.6 An eyewash/safety shower should be located nearby and a self-contained breathing apparatus should be readily available for emergency use.

4.7 Exposure to chemicals used in this procedure must be controlled at or below levels set by governmental authorities (e.g., Occupational Safety and Health Administration's [OSHA] permissible exposure limits [PEL] as found in 29 CFR 1910.1000; see www.osha.gov for latest

version). In addition, the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) comprised of time weighted averages (TLV-TWA), short term exposure limits (TLV-STEL) and ceiling limits (TLV-C) are recommended as a general guide for air contaminant exposure which should be met (see 14.1).

5. Reagents

- 5.1 Acetic acid, 1.0N (CH_3COOH)
- 5.2 Cupric nitrate 2.5 hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$)
- 5.3 Ethylene diaminetetraacetic acid (free acid) (EDTA) ($\text{C}_{10}\text{H}_{16}\text{O}_8\text{N}_2$)
- 5.4 Methanol
- 5.5 1-(2-Pyridylazo)-2-naphthol, (PAN) ($\text{C}_{15}\text{H}_{11}\text{ON}_3$)
- 5.6 Sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$)
- 5.7 Sodium hydroxide, 1.0N (NaOH)

6. Sampling

6.1 Conduct the test in triplicate; i.e., analyze 3 test specimens from a sample.

7. Specimens

7.1 Do not use aluminum or metallic weighing pans.

7.2 For analysis of solid EDTA, HEDTA, and DTPA (either free acid or salt forms) weigh a 0.24-0.26 g specimen of the dried chelating agent to an accuracy of 0.01 g.

7.3 For analysis of commercial solution, of salts of the chelating agents, weigh a 0.49-0.51 g specimen of the solution to an accuracy of 0.01 g.

8. Conditioning

8.1 If solid chelating agent is being evaluated, dry a 2-g sample at the appropriate temperature for at least 2 h and cool in a desiccator before weighing specimens.

8.2 Dry free acid forms of chelating agents at 120°C.

8.3 Dry salt forms of chelating agents at 80°C.

9. Preparation of Reagents

9.1 Cupric Nitrate Solution: Dissolve 23.30 g of cupric nitrate 2.5 hydrate and dilute to 1.000 L in a volumetric flask.

Calculate the molarity of the cupric nitrate solution (see 11.1).

9.2 PAN Indicator: Dissolve 0.025 g of 1-(2-pyridylazo)-2-naphthol in 50 mL of methanol. Store in a refrigerator in a stoppered bottle. Prepare fresh weekly.

9.3 Acetate Buffer Solution: (pH = 4.65). Dissolve 34.0 g of sodium acetate trihydrate in 500 mL of water and add 15 mL of glacial acetic acid. Mix well and store in a closed container.

9.4 Standardization of Copper-Nitrate Solution: Weigh to the nearest 0.0001 g approximately 0.5 g of pure reagent grade EDTA acid powder into each of the three 250-mL Erlenmeyer flasks. Add 150 mL of distilled water and 6.5 mL of 1.0*N* sodium hydroxide (or five drops of 50% sodium hydroxide) and stir the mixture until the EDTA is dissolved. Add 25 mL of sodium acetate buffer. Adjust to pH 4.5-5.5 with 1.0*N* acetic acid or 1.0*N* sodium hydroxide, if necessary. Add 1 mL PAN indicator and titrate immediately with copper nitrate to a permanent purple end point. Calculate the molarity of copper using Equation 1:

$$M = \frac{(W)(P)(K)}{V} \quad (\text{Eq. 1})$$

where:

M = Molarity of copper nitrate, expressed in moles/L
 W = Weight of EDTA acid in grams
 P = Percent purity of EDTA acid
 V = Volume of copper nitrate titrant in mL

$$\begin{aligned} K &= 0.042994 \\ &= \frac{(1000) \text{ mL/L}}{(100)(232.59 \text{ g/mole})} \\ &= 0.042994 \frac{\text{mole} - \text{mL}}{\text{g} - \text{L}} \end{aligned}$$

10. Procedure

10.1 Quantitatively transfer the specimen to a 500-mL Erlenmeyer flask and add 150 mL of water (see 7.1, 7.2 and 7.3). Wash any residual chelating agent from the weighing paper or dish into the flask, and swirl to mix (dissolve).

10.2 Add 25 mL of pH 4.65 acetate buffer solution to the flask and swirl to mix. Check the pH and adjust to 4.5-5.5 with 1.0*N* acetic acid or 1.0*N* sodium hydroxide, if necessary.

10.3 Add 1 mL of PAN indicator to the flask and swirl to mix.

10.4 Titrate with 0.1000 M cupric nitrate solution to a purple end point that persists for at least 1 min.

11. Calculation

11.1 Calculate the CaCV for each specimen to 3 significant digits for each titration using the Equation 2:

$$\text{CaCV} = \frac{(100.1)(V)(M)}{W} \quad (\text{Eq. 2})$$

where:

CaCV = Calcium chelation value, expressed as mg CaCO₃/g chelating agent
 V = Volume of cupric nitrate titrant in mL

M = Molarity of cupric nitrate solution, expressed in mmoles/mL
 100.1 = Molecular weight of calcium carbonate, expressed in mg/mole

11.2 Average the CaCV values for the 3 specimens tested.

12. Report

12.1 Report for each sample tested:

12.1.1 A description or identification of the sample.

12.1.2 Evaluation was performed using AATCC TM168-2018e.

12.1.3 Average CaCV, to 3 significant digits.

12.1.4 Any modifications of the test method.

13. Precision and Bias

13.1 *Precision*. The intralaboratory, single operator, single apparatus, same day precision of the test method is ± 2 (1.60) standard deviations. The interlaboratory precision of the test method (over five participating laboratories) is ± 1 (0.54) standard deviations.

13.2 *Bias*. Chelation value can be defined only in terms of a test method. There is no independent method for determining the true value. As a means of estimating this property, the method has no known bias.

14. Notes

14.1 Available from Publications Office, ACGIH, Kemper Woods Center, 1330 Kemper Meadow Dr., Cincinnati OH 45240; +1.513.742.2020; www.acgih.org.