

Test Method for Chelation Value of Aminopolycarboxylic Acids and Their Salts: Calcium Oxalate

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Foreword

The titration in this method 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. An alternative procedure, excluding the effect of partially-substituted products, is provided in AATCC TM168, Test Method for Chelation Value of Polyaminopolycarboxylic Acids and Their Salts: Copper PAN.

1. Purpose and Scope

1.1 The active 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.

2. Principle

2.1 The chelation value is determined experimentally by titrating a weighed sample of chelating agent with a calcium ion solution of known concentration. A precipitating anion (oxalate) is present during the titration. As the calcium solution is added, the ions are chelated by the chelating agent and no permanent precipitate is formed as long as there is free chelating agent present. Beyond this point, any excess calcium ion that is added reacts with oxalate anion to form a cloudy precipitate which is the endpoint.

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 hydrochloric acid and sodium hydroxide use chemical goggles or face shield, impervious gloves and an impervious apron. Concentrated acids should be handled only in an adequately ventilated laboratory hood. CAUTION: Always add acid to water.

4.4 Diethylamine hydrochloride is an eye, skin and respiratory irritant. It should be handled only in an adequately ventilated hood.

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

4.6 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 15.1).

5. Uses and Limitations

5.1 Analysis by this method will yield a CaCV that includes partially-substituted EDTA, HEDTA and DTPA as well as nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), glycolate and other weak chelating agents. These compounds may be present in some commercial products.

5.2 AATCC TM168 is an alternative procedure that yields a CaCV that does not include the partially-substituted products and weaker chelating agents.

6. Reagents

- 6.1 Calcium carbonate (CaCO_3).
- 6.2 Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$).
- 6.3 Diethylamine hydrochloride [$(\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl}$]
- 6.4 Sodium hydroxide (NaOH) solution, 50% W/W.
- 6.5 Hydrochloric acid (HCl) conc.

7. Sampling

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

8. Specimens

8.1 Do not use aluminum or metallic weighing pans.

8.2 For analysis of solid EDTA, HEDTA and DTPA (either free acid or salt forms) weigh a 0.49-0.51 g specimen of the dried chelating agent to an accuracy of 0.01 g.

8.3 For analysis of commercial solutions of salts of the chelating agents in 8.2 weigh a 1.00-1.20 g specimen of the solution to an accuracy of 0.01 g.

9. Conditioning

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

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

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

10. Preparation of Reagents

10.1 Calcium Titrant Solution (0.250 M): Weigh 25.0 g of calcium carbonate to an accuracy of 0.1 g and add it to 300 mL of water in a 600-mL beaker with

stirring on a magnetic stirrer. Dissolve by adding 43 mL of concentrated hydrochloric acid. Add the hydrochloric acid slowly and carefully to prevent bubbling over and excessive splattering. After the calcium carbonate has dissolved (the solution becomes clear), heat the solution to boiling and allow it to boil for at least 5 min to expel carbon dioxide. Cool the solution to room temperature, transfer it to a 1-L volumetric flask and dilute it to 1 L. Prepare a fresh solution monthly.

10.2 Sodium Oxalate Indicator: Dissolve 5 g of sodium oxalate in 250 mL of water. Prepare a fresh solution monthly.

10.3 Sodium Hydroxide (50%): 50% solution (W/W) of sodium hydroxide is available from many laboratory supply vendors. It can be prepared by dissolving 100 g of sodium hydroxide pellets in 100 mL of water in a polyethylene bottle. Let stand for a week to allow the insoluble sodium carbonate to settle.

10.4 pH 12.0 Buffer Solution: Dissolve 41.0 g of diethylamine hydrochloride in 400 mL of water. Add 40 mL of 50% sodium hydroxide and dilute to 500 mL. Store in a polyethylene bottle. Prepare a fresh solution monthly.

11. Procedure

11.1 Pour the specimen into a 250-mL Erlenmeyer flask and add 85 mL of water. Wash any residual chelating agent from the weighing paper or dish into the flask.

11.2 Add 5 drops of 50% sodium hydroxide (10 drops if the free acid form of a chelating agent is being analyzed) and swirl to dissolve and/or mix the chelating agent.

11.3 Add 1 mL of pH 12.0 buffer solution and swirl to mix.

11.4 Add 10 mL of sodium oxalate solution and swirl to mix.

11.5 Using a 10-mL burette, titrate with calcium titrant solution until a drop produces a slight turbidity that persists for at least 30 s (see 15.2).

12. Calculation

12.1 Calculate the CaCV for each specimen to 3 significant digits using Equation 1:

$$\text{CaCV} = \frac{(100.1)(0.250)(V)}{W} \quad (\text{Eq. 1})$$

where:

CaCV = Calcium chelation value, expressed as mg CaCO_3 /g chelating agent

100.1 = Molecular weight of CaCO_3 expressed in mg/mole

0.250 = Molarity of calcium titrant solution expressed in mmoles/mL

V = Volume of calcium titrant solution in mL

W = Weight of specimen in grams

12.2 Average the CaCV values for the 3 specimens tested.

13. Report

13.1 Report for each sample tested:

13.1.1 A description or identification of the sample.

13.1.2 Evaluation was performed using AATCC TM 149-2018e.

13.1.3 Average CaCV, to 3 significant digits.

13.1.4 Any modifications of the test method.

14. Precision and Bias

14.1 *Summary.* An interlaboratory study was conducted in March 1990 to

establish the precision of the test method. Four chelating agents (EDTA, tetrasodium salt; EDTA, 40% solution of tetrasodium salt; DTPA, free acid; and DTPA, 40% solution) were evaluated.

14.2 *Precision.* The components of variance as standard deviations of CaCV were calculated as follows:

Single Operator Component	1.46
Interlaboratory Component	0.00

14.3 *Critical Differences.* For the components of variances reported in 13.2, two averages of observed values should be considered significantly different at the 95% probability level if the difference is equal to or exceeds the following critical differences:

Single Operator	4.04
Interlaboratory	4.04

14.4 *Bias.* Based on the theoretical calcium chelation values of the four materials used in the interlaboratory study, the average bias of the five laboratories was 2.24%. The individual biases for the four materials and five laboratories ranged from 2.50-4.25%.

15. Notes

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

15.2 Turbidity is easier to observe when a piece of black paper is placed beneath and behind the flask, and the flask is illuminated from the side by a white fluorescent light. Add the calcium titrant dropwise once the turbidity begins to persist for more than 2-3 s. The endpoint is the first sign of turbidity that persists for at least 30 s. If there is uncertainty as to whether a slight turbidity has been obtained, compare the appearance of the flask to that of one containing only water, which has a distinct clear appearance.