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Designation: D4954 – 89 (Reapproved 2017)

Standard Test Method for Determination of Nitrilotriacetates in Detergents[1]

This standard is issued under the fixed designation D4954; 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 describes the determination of nitrilotriacetates (NTA) in 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.* For specific safety precautions, see 6.5.

2. Summary of Test Method

2.1 A known excess amount of copper nitrate solution is added to the detergent sample under controlled pH conditions. The uncomplexed copper is back-titrated potentiometrically with a standard NTA solution using a copper ion specific electrode. The millimoles of NTA in the sample are equivalent to the millimoles of copper added, less the millimoles of the NTA titrant.

3. Significance and Use

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

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

4. Interferences

4.1 The presence of substances that will make copper complex like citrate, formate, ethylenediaminetetraacetate, and phosphonate, will interfere positively in the determination of NTA.

5. Apparatus

5.1 *Volumetric Flasks,* 200-mL, 500-mL, 1000-mL.

5.2 *Beakers,* 200-mL (tall form), 250-mL, 1000-mL.

5.3 *Pipets,* 25-mL, 100-mL.

5.4 *Graduated Cylinders,* 10-mL, 25-mL.

5.5 *Copper Ion Electrode (Orion Model 94-29).*

5.6 *Single Junction Reference Electrode (Orion Model 90-01),* filled with Orion 90-00-01 solution.

5.7 *pH Combination Electrode.*

5.8 *Burets,* 10-mL, 25-mL, 50-mL.

5.9 *pH Meter,* with millivolt capabilities.

5.10 *Automatic Titrator*—may be substituted for 5.8 and 5.9.

5.11 *Magnetic Stirrer/Hot Plate.*

5.12 *Balance,* with 1-mg sensitivity.

6. Reagents

6.1 *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.[2] Other grades may be substituted, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Disodium Ethylenediaminetetraacetate (EDTA),* 0.1 M.[3]

6.3 *Nitric Acid,* concentrated.

6.4 *Sodium Hydroxide,* 50 % reagent solution.

6.5 *Sodium Hydroxide,* 20 % solution. Mix 40 g of the 50 % solution with 60 g of water. Cool. Wear a face shield during mixing.

6.6 *Cupric Nitrate,* 0.1 M. Weigh (to the nearest 0.1 g) 6.3 g of copper metal and transfer into a 600-mL beaker. Add about 100 mL of water. Place a magnetic bar into the beaker and

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[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.

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[2] American Chemical Society, 1155 16th St., NW, Washington, DC 20036.

[3] EDTA solution is available from J. T. Baker Inc., already standardized against NIST Reference Material Calcium Carbonate.

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place on a stirrer/hotplate. Add 30 mL of concentrated nitric acid while stirring and heat gently. Stir until the copper metal dissolves. Add more nitric acid if undissolved metal remains. After dissolution, cool and transfer quantitatively to a 1-L volumetric flask. Dilute to the mark and mix the solution well.

6.6.1 Alternatively, weigh out (to the nearest 1 g) 23 g of reagent grade cupric nitrate, 2½ hydrate crystals, and transfer to a 600-mL beaker. Add 400 mL of water. Stir to dissolve the crystals and add 5 mL of concentrated nitric acid. Transfer to a 1-L volumetric flask, dilute to the mark and mix well.

6.7 *Trisodium Nitrilotriacetate Monohydrate (NTA),* 0.3 M. Weigh out (to the nearest 1 g) 41 g of NTA and dissolve in 400 mL of water in a 600-mL beaker. Transfer to a 500-mL volumetric flask, dilute to the mark and mix well.

6.8 *Sodium Acetate Buffer Solution,* Dissolve 68 g of reagent sodium acetate, trihydrate, in 500 mL of water in a 1-L beaker. Add 30 g of glacial acetic acid. Transfer to a 1-L volumetric flask, dilute with water to the mark and mix well. The pH of this solution should be 4.6 to 4.8.

7. Standardization of 0.1-M Cupric Nitrate

7.1 Add 50 mL of water into a 200-mL tall form beaker. Add 3 mL of concentrated nitric acid from a graduated cylinder. Transfer by pipet a 25-mL aliquot of the cupric nitrate solution into the beaker.

7.2 Place the pH combination electrode into the solution. Adjust the pH to 1.0 to 1.1 by dropwise addition of 50 % NaOH solution. About 2 mL may be required. Towards the end, use the 20 % NaOH solution.

7.3 Add 25 mL of the sodium acetate buffer solution from a graduated cylinder. Adjust the pH to 4.6 to 4.7 by dropwise addition of the 20 % NaOH solution. Cool to room temperature in a cold water bath.

7.4 Bring the solution to the titration assembly and immerse the copper and single junction electrodes. Stir the solution. With the meter set for mV reading, begin titrating with the 0.1 M standard EDTA using a 25 or 50-mL buret. The first 22 mL of titrant can be added rapidly.

7.5 Add 0.5-mL increments and record the mV readings after each addition. It may take 1 to 2 min to obtain stable readings at the endpoint region. Determine the endpoint in accordance with Table 1.

7.6 Calculate the molarity of the cupric nitrate solution as follows:

$$\text{Molarity of Cupric Nitrate} = (M \times V)/25 \qquad (1)$$

where:

M = molarity of EDTA, and
V = mL of EDTA.

8. Standardization of NTA Solution

8.1 Proceed as for the standardization of the 0.1-M cupric nitrate; except in this case, the titrant will be the NTA solution rather than EDTA solution. Use a 10-mL buret for the NTA titrant.

TABLE 1 Determination of Inflection Point[A]

NOTE 1—Volume of NTA required to react with 25 mL of cupric nitrate solution (0.0972 M).

	NTA, mL	mV, (+)			
	0	303			
	1.00	300			
	2.00	297			
	3.00	294			
	4.00	291			
	5.00	287			
	6.00	283			
	7.00	275	ΔmV	Δ(ΔmV)	
	7.50	270			
			10		
V_1	8.00	260		36	D_1
			46		
V_2	8.50	214		25	D_2
			21		
	9.00	193			
	9.50	188			
	10.00	186			

[A] End Point = $V_1 + [(V_2 - V_1) \times (D_1/(D_1 + D_2))]$.
= 8.00 + [(8.50 − 8.00) × (36 ⁄(36 + 25))].
= 8.00 + [(0.5) × (0.59)].
= 8.00 + 0.30.
= 8.30 mL.
Then,

$$\text{Molarity of } NTA = \frac{25.00 \text{ mL cupric nitrate} \times 0.0972\ M}{8.30 \text{ mL } NTA} = 0.2928\ M$$

8.2 The first 6 mL can be added rapidly, then continue with 0.5-mL increment additions. Determine the endpoint in accordance with Table 1.

8.3 Calculate the molarity of the NTA as follows:

$$\text{Molarity of } NTA = (V_1 \times M)/V_2 \qquad (2)$$

where:

V_1 = mL of cupric nitrate,
M = molarity of cupric nitrate, and
V_2 = mL of NTA.

9. Procedure

9.1 Weigh to the nearest milligram 10 g of detergent and slurry in water. Reduce the sample size accordingly if the NTA content is greater than 25 %. Transfer to a 500-mL volumetric flask, dilute to the mark, and stir to mix well.

9.2 While stirring the sample, pipet out a 100-mL aliquot and transfer into a 250-mL tall form beaker.

9.3 Add 3 mL of concentrated nitric acid from a 10-mL graduated cylinder while stirring. Let the sample set for 5 min. Place the pH combination electrode in the sample, then continue adding the nitric acid while stirring until pH equals 0.

9.4 Add 25 mL of the standard 0.1-M cupric nitrate solution from a pipet into the sample while stirring.

9.5 Adjust the pH to 1.0 to 1.1 by dropwise addition of the 50 % or the 20 % NaOH solution as required.

9.6 Add 25 mL of sodium acetate buffer solution using a 25-mL graduated cylinder while stirring. Adjust pH to 4.6 to 4.7 with 20 % NaOH solution.

9.7 Rinse the electrodes with water into the sample beaker. Cool the sample to room temperature in a cold water bath.

9.8 Place the copper electrode and single junction reference electrode into the sample. Turn the meter to the mV mode.

9.9 Titrate with the NTA solution using a 10-mL buret. It may take a few minutes at the start to attain a stable reading. Add the titrant in 0.5-mL increments and record the mV reading after each addition. Add at least two increments past the break point.

9.10 Determine the endpoint in accordance with Table 1.

10. Calculation

10.1 Calculate the percentage of $Na_3NTA \cdot H_2O$ as follows:

$$\%\ \text{weight of}\ Na_3NTA \cdot H_2O \tag{3}$$

$$= ([(A \times M_1) - (B \times M_2)] \times 0.275 \times 100)/W$$

where:

A = mL of cupric nitrate added to the sample,
M_1 = molarity of cupric nitrate,
B = mL of NTA titrant,
M_2 = molarity of NTA titrant, and
W = weight of sample, in grams, present in aliquot.

11. Precision and Bias

11.1 *Precision:*

11.1.1 In this study, two detergent samples with average NTA contents, 14.93 and 10.02 weight %, were determined. Each sample was analyzed in duplicate, twice, by a given analyst. Each duplicate analysis was done on a different day.

11.1.2 *Repeatability (Single Analyst)*—The pooled standard deviation of results (each the average of duplicates) for two samples obtained by the same analyst on different days, has been estimated to be 0.24 weight % at 12 df. Two such averages should be considered suspect (95 % confidence level) if they vary by more than 0.74 weight % absolute.

11.1.3 *Reproducibility (Multilaboratory)*—The pooled standard deviation of results (each the average of duplicates) for the two samples obtained by analysts in different laboratories, has been estimated to be 0.45 weight % at 10 df. Two such averages should be considered suspect (95 % confidence level) if they vary by more than 1.4 weight % absolute.

11.1.4 *Checking Limits for Duplicates*—Report the NTA content of the sample to the nearest 0.1 weight %. Duplicate runs that agree within 0.7 weight % are acceptable for averaging (95 % confidence level).

11.2 *Bias*—No statement of bias can be made for this test method, since no accepted reference material to determine the bias is available.

12. Keywords

12.1 copper ion electrode; nitrilotriacetate; NTA; titration

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