Designation: D 3989 – 01

Standard Test Method for Total Rare Earth Metals in Paint Driers by EDTA Method[1]

This standard is issued under the fixed designation D 3989; 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 the titrimetric determination of rare earth metals in liquid rare earth metal driers and utilizes the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA).

1.2 This test method is limited to the determination of the rare earth metal content of a liquid rare earth metal drier that does not contain other drier elements. The method is not applicable to drier blends.

1.3 This test method has been tested in concentrations of 6 % cerium and 6 % rare earth metals, but there is no reason to believe that it is not suitable for higher or lower drier metal concentrations provided specimen size is adjusted accordingly.

1.4 *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:*

D 600 Specification for Liquid Paint Driers[2]

D 1193 Specification for Reagent Water[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals[4]

E 300 Practice for Sampling Industrial and Specialty Chemicals[4]

3. Summary of Test Method

3.1 A diluted solution of the drier is complexed with an excess of EDTA, the pH adjusted to 5.0, and then titrated with zinc chloride solution to a xylenol orange end point.

4. Significance and Use

4.1 This test method may be used to confirm the stated content of a pure, liquid rare earth metal drier manufactured for use in the coatings industry.

5. Interferences

5.1 Calcium does not interfere at low pH.

5.2 All other cations that can be titrated with EDTA in acidic media will interfere and must not be present in the drier.

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 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.

6.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

6.3 *Ammonium Chloride—Ammonium Hydroxide Buffer Solution*—Add 350 mL of concentrated ammonium hydroxide (NH_4OH) to 54 g of ammonium chloride (NH_4Cl), and dilute to 1 L with water.

6.4 *Ammonium Hydroxide* (NH_4OH), (1+1).

6.5 *Ascorbic Acid*.

6.6 *Eriochrome Black T Indicator*—Mix and grind thoroughly in a mortar a mixture of 0.2 g of Eriochrome Black T and 100 g of sodium chloride. Store the mixture in a tightly stoppered bottle where it is stable indefinitely.

6.7 *EDTA, Standard Solution* (0.01 *M*)—Weigh about 3.73 g of disodium salt of ethylenediaminetetraacetic acid dihydrate to the nearest 0.01 g, dissolve in water, and dilute to approximately 1 L in a glass-stoppered bottle.

6.8 *Hydrochloric Acid* (HCL), (1+1).

6.9 *Isopropyl Alcohol* (99.5 %).

6.10 *Sodium Acetate-Acetic Acid Buffer Solution*—Dissolve 82 g of sodium acetate in water and dilute to 1 L. Adjust pH to 5.0 with glacial acetic acid using a pH meter.

6.11 *Xylenol Orange Indicator*—Dissolve 0.2 g in 100 mL of water. Prepare fresh daily as required.

6.12 *Zinc Chloride Solution, Standard* (0.01 *M*)—Weigh

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

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[2] *Annual Book of ASTM Standards*, Vol 06.04.

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

[4] *Annual Book of ASTM Standards*, Vol 15.05.

[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.

about 0.65 g of zinc ribbon (Note 1) to the nearest 5 mg on a glazed paper. Transfer to a 1-L volumetric flask and add 25 mL of dilute hydrochloric acid (1 + 3). Warm if necessary on a steam bath to dissolve the material completely. Cool, dilute to the mark with water, and mix thoroughly.

NOTE 1—Store the zinc ribbon in a tight container to prevent the surface of the zinc from oxidizing.

7. Sampling

7.1 Take a small sample of liquid drier from bulk using the procedure in Practice E 300 appropriate for the size of the container, Section 19 for tanks and tank cars or Section 23 for drums and cans.

NOTE 2—Liquid driers are normally homogeneous so that only simple physical tests, such as specific gravity or solids content, on top and bottom samples from tanks are required to confirm that separation has not occurred. Agitate the drums in accordance with 23.3 of Practice E 300.

7.2 Examine the sample of drier for sediment or suspended matter which if present is evidence of noncompliance with 3.3 of Specification D 600.

7.3 If the sample is homogeneous keep it in a stoppered vessel to prevent solvent evaporation prior to analysis.

8. Standardization

8.1 *Zinc Chloride Solution, Standard* (0.01 *M*)—Calculate the molarity, M_1, of the zinc chloride ($ZnCl_2$) solution as follows:

$$M_1 = S_1/65.37 \quad (1)$$

where:
M_1 = molarity of $ZnCl_2$ solution,
S_1 = grams of zinc used, and
65.37 = grams of zinc per litre to produce a 1 M solution.

8.2 *EDTA Solution, Standard* (0.01 *M)*—Transfer 40.00 mL of this solution from a buret into a 250-mL assay beaker or wide-mouth flask. Add 50 mL of isopropyl alcohol, 10 mL of ammonium chloride-ammonium hydroxide buffer solution, and about 0.2 g of Eriochrome Black T indicator mixture (Note 3). Mix thoroughly by swirling. Titrate with the standard $ZnCl_2$ solution to the first permanent appearance of a red color.

NOTE 3—If the end point is overstepped, add 1.0 mL of the EDTA solution to the mixture and titrate again with standard $ZnCl_2$ solution. Use total volume of each solution for the calculation.

8.2.1 Calculate the molarity, M_2, of the EDTA solution as follows:

$$M_2 = V_1M_1/V_2 \quad (2)$$

where:
V_1 = volume of $ZnCl_2$ solution, mL,
M_1 = molarity of $ZnCl_2$ solution,
V_2 = volume of EDTA solution, mL, and
M_2 = molarity of EDTA solution.

9. Procedure

9.1 Check the clarity of the drier. If not clear, centrifuge a portion of the sample until it is clear, keeping the centrifuge tube stoppered to prevent solvent evaporation.

9.2 Place a few grams of the drier in a 50-mL Erlenmeyer flask fitted with a cork, through which passes a dropping tube and a rubber bulb (or medicine dropper) and obtain the total weight. Into a 400-mL beaker weigh by difference to the nearest 0.5 mg the following specimen sizes: (*a*) 0.5 to 0.7 g for 6 % rare earth metals or cerium, (*b*) 0.25 to 0.35 g for 12 % rare earth metals, and (*c*) proportionate amounts for more or less rare earth metals or cerium.

9.3 Add about 5 mL of isopropyl alcohol and 2 mL of dilute HCl. Warm on a hot plate until the specimen dissolves.

9.4 While still warm, add 0.4 to 0.5 g of ascorbic acid to reduce Ce (IV) and warm until any yellow color disappears. Add 70 mL of isopropyl alcohol and 40.0 mL of EDTA solution.

9.5 Place on the magnetic stirrer and add a stirring bar and the electrodes from the pH meter. Adjust the pH to approximately 4.0 with 1 + 1 NH_4OH, add 25 mL of sodium acetate buffer, and adjust pH to 5.0 with 1 + 1 NH_4OH or 1 + 1 HCl.

9.6 Add approximately 1 mL of xylenol orange solution and titrate with standardized zinc chloride solution from a yellow to orange end point.

NOTE 4—Use a good titration light to assist in detecting the end point.

10. Calculation

10.1 Calculate the percent total rare earth metals, *T*, present as follows:

$$T = (V_3M_2 - V_4M_1)14.0/S_2 \quad (3)$$

where:
V_3 = volume of EDTA solution, mL,
M_2 = molarity of EDTA solution,
V_4 = volume of $ZnCl_2$ solution, mL,
M_1 = molarity of $ZnCl_2$ solution,
14.0 = millimolar weight of rare earth metals × 100, and
S_2 = grams of specimen used.

11. Precision and Bias [6]

11.1 *Precision*—The precision estimates are based on an interlaboratory study in which one operator in five different laboratories analyzed in duplicate on two different days samples of 6 % rare earth metal drier and 6 % cerium drier. The driers were commercially supplied. The results were analyzed statistically in accordance with Practice E 180 and the within-laboratory coefficient of variation was found to be 0.4 % relative at 10 df and the between-laboratory coefficient of variation was 1.6 % relative at 8 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 1.25 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 5.3 % relative.

[6] Supporting data are available from ASTM Headquarters. Request RR: D01-1030.

11.2 *Bias*—Bias cannot be determined because there are no accepted standards for rare earth metals in paint driers.

12. Keywords

12.1 analysis rare earth drier; EDTA; paint driers