Designation: D3969 – 01 (Reapproved 2012)

Standard Test Method for Zirconium in Paint Driers by EDTA Method[1]

This standard is issued under the fixed designation D3969; 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 zirconium in zirconium driers used in the coatings industry and utilizes the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA).

1.2 This test method is limited to the determination of the zirconium content of a liquid zirconium drier that does not contain other drier elements. The test method is not applicable to drier blends and does not differentiate hafnium from zirconium.

1.3 All cations that can be titrated with EDTA in acid media interfere and must not be present in the sample.

1.4 This test method has been tested for concentrations of 6 and 12 % zirconium, but there is no reason to believe that it is not suitable for higher or lower zirconium concentrations, provided specimen size is adjusted proportionately.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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:*[2]

D600 Specification for Liquid Paint Driers

D1193 Specification for Reagent Water

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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E300 Practice for Sampling Industrial Chemicals

3. Summary of Test Method

3.1 The zirconium drier is digested with concentrated sulfuric acid and 30 % hydrogen peroxide to destroy all organic matter. The diluted solution is boiled with an excess of EDTA, the pH adjusted, and the excess titrated with bismuth nitrate using xylenol orange as the indicator.

4. Significance and Use

4.1 The amount of zirconium drier used in oxidizing-type coatings significantly affects their drying properties. This test method may be used to confirm the stated content of a pure liquid zirconium drier manufactured for use by the coatings industry.

5. Apparatus

5.1 *Centrifuge,* capable of developing 1000 to 2000 g.

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.[4] 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, references to water shall be understood to mean reagent water conforming to Type II of Specification D1193.

6.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated, ammonium hydroxide (NH_4OH).

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[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 Paints and Paint Materials.

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[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] *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.

6.4 *Bismuth Nitrate, Standard Solution (0.05 M)*—Dissolve 24.25 g of bismuth nitrate ($Bi(NO_3)\cdot 5H_2O$) in 20 to 30 mL of concentrated nitric acid (use a magnetic stirrer if possible). After solution is complete, dilute to 1 L with water.

NOTE 1—Add the water very slowly to the acid solution, while cooling the flask in an ice bath to prevent splattering.

6.5 *EDTA, Standard Solution(0.05 M)*—Dissolve 18.61 g of EDTA in 300 to 500 mL of water and dilute to 1 L. Store in a polyethylene or borosilicate glass bottle.

6.6 *Eriochrome Black-T Indicator*—Triturate 0.100 g of powdered Eriochrome Black-T with 100 g of sodium chloride (NaCl), and store the mixture in a tightly stoppered bottle. This mixture remains stable for several years.

6.7 *Formic Acid* (sp gr 1.22, 90 %) HCOOH.

6.8 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

6.9 *Hydrogen Peroxide* (30 %).

6.10 *Isopropyl Alcohol* (99.5 %).

6.11 *Nitric Acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

6.12 *Phenolphthalein Indicator (1.0 %)*—Dissolve 1.0 g of phenolphthalein indicator in 100 mL of methanol, ethanol, or isopropanol.

6.13 *Sodium Sulfite* (Na_2SO_3).

6.14 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

6.15 *Xylenol Orange (0.2 %)*—Dissolve 0.2 g in 100 mL of water. Prepare fresh each day used.

6.16 *Zinc Chloride, Standard Solution (0.100 M)*—Dissolve 6.538 g of zinc ribbon (Note 2) in concentrated HCl, keeping the excess of acid as small as possible. After the zinc has dissolved, cool to room temperature and dilute to 1 L in a volumetric flask.

NOTE 2—Store the zinc ribbon in a tightly closed 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 E300 appropriate for the size of the container: section on Bottle Sampling for tanks and tank cars, or section on Tube Sampling for drums and cans.

NOTE 3—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 drums in accordance with section on Tube Sampling in Practice E300.

7.2 Examine the sample of drier for sediment or suspended matter which, if present, is evidence of noncompliance with Specification D600.

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, Standard Solution (0.100 M)*—Calculate the molarity, M_1, of the zinc chloride ($ZnCl_2$) solution as follows:

$$M_1 = \frac{S_1}{65.37} \quad (1)$$

where:

S_1 = zinc used, g, and
65.37 = zinc to produce a 1 M solution, g/L.

8.2 *EDTA, Standard Solution (0.05 M)*—Pipet 20 or 25-mL portions (use calibrated pipets) of the standard $ZnCl_2$ solution into a 250-mL Erlenmeyer flask. Add concentrated NH_4OH dropwise until the precipitate which forms redissolves. Add 3 mL more of NH_4OH. Add 0.20 to 0.25 g Eriochrome Black-T indicator mixture and titrate with EDTA until the solution changes from red to clear blue.

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

$$M_2 = V_1 M_1 / V_2 \quad (2)$$

where:

V_1 = volume of $ZnCl_2$ solution, mL, and
V_2 = volume of EDTA solution, mL.

8.3 *Bismuth Nitrate, Standard Solution (0.05 M)*—Pipet 24 mL of 0.05 *M* EDTA into a 250-mL Erlenmeyer flask, add 75 mL of distilled water, neutralize with concentrated NH_4OH to a pink end point with phenolphthalein, and then add 15 mL of concentrated formic acid. After cooling to room temperature, titrate with 0.05 *M* bismuth nitrate solution and xylenol orange from a yellow to a pink end point.

8.3.1 Calculate the molarity, M_3, of the $Bi(NO_3)_3$ solution as follows:

$$M_3 = \frac{V_3 M_2}{V_4} \quad (3)$$

where:

M_3 = molarity of $Bi(NO_3)_3$ solution,
V_3 = 24.0 mL
M_2 = molarity of EDTA solution, and
V_4 = volume of $Bi(NO_3)_3$ solution, mL.

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 rubber bulb (or a medicine dropper) and obtain the total weight. Into another Erlenmeyer flask, weigh by difference to 0.5 mg, a specimen of the appropriate size: (*a*) 0.6 to 0.7 g for 6 % Zr, (*b*) 0.3 to 0.35 g for 12 % zirconium, and (*c*) proportionate amounts for more or less Zr. Add several glass beads, 5 mL of concentrated H_2SO_4, and 10 mL of 30 % H_2O_2 and heat on the hot plate until white fumes appear. Destroy all the organic matter by further additions of hydrogen peroxide in 10-mL increments.

9.3 Cool (25 to 30°C), add 75 mL of water, not less than 0.2 g of Na_2SO_3 and boil for 5 min (Note 4). Add to the warm solution 25 mL of 0.05 *M* EDTA and heat to boiling.

NOTE 4—If the solution turns milky red after the addition of Na_2SO_3, boiling will make it clear. Sometimes a black precipitate forms at this time also. Disregard it since it does not interfere with the endpoint.

9.4 Allow the solution to cool and neutralize with concentrated NH_4OH to a pink end point using phenolphthalein indicator. Add 15 mL of concentrated formic acid and after cooling to room temperature in an ice bath, add 6 to 8 drops of xylenol orange and titrate with standard $Bi(NO_3)_3$ solution from a yellow to a pink end point.

NOTE 5—Because the color of metal indicators (and some of their metal complexes) is affected by pH changes, the pH must be kept constant during titration by the recommended buffer during the titration.

10. Calculation

10.1 Calculate the percent of metal, *A*, (Note 6) present as zirconium as follows:

$$A = \left(V_4 M_2 - V_5 M_3\right) \frac{9.122}{S_2} \quad (4)$$

where:

V_4 = volume of EDTA solution, mL.
V_5 = volume of $Bi(NO_3)_3$ solution, mL,
9.122 = millimolar weight of zirconium × 100, and
S_2 = specimen weight, g.

NOTE 6—Zirconium driers may contain up to 5 % of the total metal as hafnium. However, the typical hafnium content would be 1.6 ± 0.1 % of the total metal present. The rest would be zirconium. Based on supplier results, there is no difference in the activity of hafnium versus zirconium in paints.

11. Precision and Bias[5]

11.1 *Precision*—The precision estimates are based on an interlaboratory study in which one operator in six different laboratories analyzed in duplicate on two different days two samples of zirconium drier containing 6 and 12 % zirconium. The zirconium drier was a commercially supplied sample. The results were analyzed statistically in accordance with Practice E180, and the within-laboratory coefficient of variation was found to be 0.46 % relative at 12 df and the between-laboratories coefficient of variation was 1.61 % relative at 10 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence levels:

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 1.42 % 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 5.0 % relative.

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

12. Keywords

12.1 analysis; EDTA method; liquid driers; paint driers; zirconium drier

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1031.