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100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Vanadium in Paint Driers by EDTA Method[1]

This standard is issued under the fixed designation D 3988; 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 vanadium in liquid vanadium driers and utilizes the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA).

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

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

1.4 This test method has been tested for concentrations of 3 and 4 % vanadium, but there is no reason to believe that it is not suitable for higher or lower vanadium concentrations provided specimen size is adjusted proportionately.

1.5 *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 Chemicals[4]

E 300 Practice for Sampling Industrial Chemicals[4]

3. Summary of Test Method

3.1 The amount of vanadium drier used in oxidizing-type coatings significantly affects their drying properties. The vanadium drier is acidified and heated to make the vanadium available for chelation with EDTA. It is then chelated, the pH adjusted, and the excess titrated with zinc chloride solution, using Eriochrome Black T as the indicator.

4. Significance and Use

4.1 This test method may be used to confirm the stated content of a pure liquid vanadium 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.[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 Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

6.4 *Ascorbic Acid*.

6.5 *Buffer Solution*—Add 350 mL of concentrated NH_4OH to 54 g of ammonium chloride and dilute to 1 L with water.

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 EDTA to the nearest 0.01 g, dissolve in water, and dilute to approximately 1 L in a glass-stoppered bottle.

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

6.9 *Isopropyl Alcohol*, 99.5 %.

6.10 *Zinc Chloride, Standard Solution* ($ZnCl_2$) (0.01 *M*)—Weigh about 0.65 g of zinc (Note 1) to 5 mg. 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.

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[1] This test method is under the jurisdiction of ASTM Committee D-1 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] *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.

NOTE 1—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 E 300 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 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 the section on Tube Sampling of Practice E 300.

7.2 Examine the sample of drier for sediment or suspended matter which, if present, is evidence of noncompliance with 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, Standard Solution* (0.01 *M*)—Calculate the molarity, M_1 as follows:

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

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

8.2 *EDTA, Standard Solution* (0.01 *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 buffer solution, and about 0.2 g of indicator mixture. 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 of the EDTA solution, M_2, 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, and
V_2 = volume of EDTA 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 eye dropper) and obtain the total weight. Weigh by difference to 0.5 mg two or three 0.18 to 0.22-g specimens into 250-mL wide-mouth flasks.

NOTE 4—This is the correct specimen weight range for a vanadium drier containing 3 to 6 % of vanadium (16 to 24 mL of standard 0.01 *M* $ZnCl_2$ solution is required for the titration).

9.3 Add to each flask, 15 mL of isopropyl alcohol and 1.0 mL of concentrated HCl. Boil the solutions (use a steam bath if possible, and boiling aids) gently for 5 min, then cool for 5 to 10 min in a cold water bath (Note 5). Add 35 mL more of isopropyl alcohol to each flask.

NOTE 5—Boiling with HCl converts, bi-, tri-, and tetravalent vanadium to the relativity stable vanadyl ion, VO^{++}. The latter chelates with EDTA in a 1 to 1 molar ratio as do other metallic ions.

9.4 From a buret, measure 40.0 mL of EDTA solution into each flask. Add 0.1 g of ascorbic acid (solution should be blue) and swirl to dissolve (Note 6). Add 15 to 20 mL of buffer solution and about 0.3 g of indicator mixture (Note 7). Mix thoroughly by swirling.

NOTE 6—Ascorbic acid, a reducing agent, is added to reduce any metavanadate ion, VO_3^+, to vanadyl ion, VO^{++}.

NOTE 7—The amounts of ascorbic acid and indicator mixture are not critical. With a little experience, these may be added from the tip of a spatula.

9.5 Titrate with standard $ZnCl_2$ solution to the first permanent tinge of red (see Note 8 and Note 9). Maintain vigorous swirling during the titration to ensure thorough mixing of the two phases that may appear.

NOTE 8—The color change at the end point is from blue to blue with a red tinge. Adding more $ZnCl_2$ solution gives a violet color.

NOTE 9—Use a good titration light to assist in detecting the end point.

10. Calculation

10.1 Calculate the percent of the vanadium present, *A*, as follows:

$$A = \frac{[(V_3M_2 - V_4M_1)\ 5.10]}{S_2} \quad (3)$$

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,
5.10 = millimolar weight of vanadium × 100, and
S_2 = specimen used, g.

11. Precision [6]

11.1 The precision estimates are based on an interlaboratory study in which one operator in five different laboratories analyzed in duplicate on two different days two samples of vanadium drier containing 3 and 4 % vanadium. The vanadium drier was commercially supplied. The results were analyzed statistically in accordance with Practice E 180 and the within-laboratory standard deviation was found to be 0.025 % vanadium at 9 df and the between-laboratory standard deviation 0.07 % vanadium at 7 df. Based on these standard deviations, 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 0.08 % absolute at concentrations of 3 to 4 % vanadium.

[6] Supporting data are available from ASTM Headquarters. Request RR: D01-1029.

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 0.22 % absolute at concentrations of 3 to 4 % vanadium.

12. Keywords

12.1 EDTA-analysis; liquid drier; paint driers; vanadium drier

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