Designation: D2375 – 05 (Reapproved 2011)

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

This standard is issued under the fixed designation D2375; 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 a titrimetric determination of manganese in liquid paint driers that can be dissolved in a toluene-alcohol mixture and utilizes the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA).

1.2 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 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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:*[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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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 liquid drier is dissolved in toluene and ethyl alcohol and treated with an excess of standard EDTA solution. The excess is titrated with standard zinc chloride solution using Eriochrome Black-T as the indicator.

4. Significance and Use

4.1 The amount of manganese drier used in oxidizing-type coatings significantly affects their drying properties. This test method may be used to confirm the stated manganese content of pure liquid manganese drier soluble in toluene-alcohol and 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 Chloride* (NH_4Cl).

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

6.5 *l-Ascorbic Acid.*

6.6 *Buffer Solution*—Add 350 mL of concentrated NH_4-OH (sp gr 0.90) to 54 g of NH_4Cl and dilute to 1 L with water.

6.7 *Eriochrome Black-T Indicator*—Triturate 0.2 g of Eriochrome Black-T and 100 g of NaCl, and store the mixture in a tightly stoppered bottle. This mixture remains stable for several years.

6.8 *Ethyl Alcohol* (95 %), pure or denatured.

[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.

6.9 *EDTA, Standard Solution* (0.05 *M*)—Dissolve 18.62 g of EDTA in water and dilute to 1 L. Store in a polyethylene or borosilicate glass bottle.

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

6.11 *Sodium Chloride* (NaCl).

6.12 *Toluene.*

6.13 *Zinc, Granular.*

6.14 *Zinc Chloride, Standard Solution* (0.05 *M*)—Weigh 3.2690 g of zinc to the nearest 0.5 mg and dissolve in 50 mL of dilute HCl (14 mL of concentrated HCl (sp gr 1.19) to 36 mL of water). Warm if necessary. Dilute the zinc chloride ($ZnCl_2$) solution to 1 L in a volumetric flask.

$$M_1 = 3.2690/65.37 \quad (1)$$

where:

M_1 = molarity of $ZnCl_2$ solution, and
65.37 = zinc to produce a 1 *M* solution, g.

7. Sampling

7.1 Take a small sample of liquid drier from bulk using the procedures 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 1—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 *EDTA, Standard Solution* (0.05 *M*)—Measure 40.00 mL of the EDTA solution into a 250-mL flask that contains 10 mL of toluene and 100 mL of alcohol. Add 15 mL of buffer solution and 0.2 g of indicator mixture, and mix thoroughly. Titrate with the standard zinc chloride solution to the first permanent appearance of a red color.

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

$$M_2 = V_1 M_1/40.0 \quad (2)$$

where:

V_1 = $ZnCl_2$ solution, mL,
40.0 = EDTA solution titrated, mL.

9. Procedure

9.1 Check the clarity of the drier. If not clear, centrifuge a portion of the sample until it is clear. Keep the centrifuge tube stoppered so that solvent will not evaporate.

9.2 From a buret place a few grams of the drier in a 50-mL Erlenmeyer flask that is fitted with a cork through which a dropping tube and rubber bulb (or eye dropper) pass and obtain the total weight. Weigh by difference two or three 1-g specimens (10 drops weigh about 0.2 g) to the nearest 0.5 mg into 400-mL assay beakers or wide-mouthed flasks (Note 2). Add 10 mL of toluene to each specimen and swirl to mix. Add 100 mL of 95 % ethyl alcohol and swirl again until the specimen is dissolved and well dispersed. From a buret measure 40.0 mL of EDTA solution into each beaker. Add 0.3 g of ascorbic acid, 15 mL of buffer solution, and 0.2 g of the indicator mixture. Mix thoroughly by swirling. Titrate with the standard $ZnCl_2$ solution to the first permanent tinge of red. Maintain vigorous swirling during the titration to ensure thorough mixing of the two phases which may appear.

NOTE 2—If a magnetic stirrer is available, it is convenient to titrate in an ordinary beaker. Stirring magnetically ensures thorough mixing during the titration.

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.

10. Calculation

10.1 Calculate the percent manganese present, *A*, as follows:

$$A = [((V_2 \times M_2) - (V_3 \times M_1)) \times 5.494]/S \quad (3)$$

where:

V_2 = EDTA solution, mL,
V_3 = $ZnCl_2$ solution required for specimen, mL,
S = specimen used, g, and
5.494 = millimolar weight of manganese × 100.

11. Precision and Bias (see Practice E180)

11.1 *Precision:*

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 0.05 % manganese.

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 0.15 % manganese.

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

12. Keywords

12.1 drier analysis; EDTA method; manganese