Designation: D 3804 – 02

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

This standard is issued under the fixed designation D 3804; 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 iron in liquid iron driers soluble in isopropyl alcohol and utilizes the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA).

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

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.*

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 Chemicals[4]

3. Summary of Test Method

3.1 The liquid iron drier is diluted with isopropyl alcohol and the iron chelated with excess standard EDTA. The solution is buffered and the excess EDTA is titrated with standard zinc chloride solution to the Eriochrome Black T end point.

4. Significance and Use

4.1 This test method may be used to confirm the stated content of a liquid iron drier soluble in isopropyl alcohol and manufactured for use in the coatings industry. The content determines activity level.

5. Interferences

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

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, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

6.3 *Ammonium Hydroxide* (1+3)—Add 10 mL of concentrated ammonium hydroxide (NH_4OH, sp gr 0.90) to 30 mL water.

6.4 *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.

6.5 *EDTA, Standard Solution* (0.01 *M*)—Weigh to 10 mg about 3.73 g of the disodium salt of ethylenediaminetetraacetic acid dihydrate (EDTA), dissolve in water, and dilute to approximately 1 L in a polyethylene or borosilicate glass bottle.

6.6 *Hydrochloric Acid* (1+3)—Add 3 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 9 mL of water.

6.7 *Eriochrome Black-T Indicator*—Titrate 0.20 g of the concentrated dye with 100 g of NaCl and store in a tightly stoppered jar. This mixture remains stable for several years.

6.8 *Isopropyl Alcohol* (99.5 %).

6.9 *Zinc Chloride, Standard Solution* (0.01 *M*)—Weigh to 0.5 mg about 0.65 g of zinc (Note 1) onto a glazed paper. Transfer to a 1-L volumetric flask and add 25 mL of dilute HCl (7+18) (add 7 mL of concentrated acid (sp gr 1.19) to 18 mL of water). Warm if necessary on a steam bath to dissolve completely. Cool, dilute to the mark with water and mix

[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] *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.

thoroughly. Calculate the exact molarity of this approximately 0.01-*M* solution as follows:

$$M_2 = W/65.4 \quad (1)$$

where:
M_2 = molarity of $ZnCl_2$ solution, and
W = zinc used, g.
65.4 = atomic weight of zinc.

NOTE 1—Zinc ribbon cut into small pieces with clean scissors is preferred. Granular (20 mesh) zinc requires several hours of heating on a steam bath for complete solution. Store the zinc ribbon in a tightly sealed 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 procedures in Practice E 300 appropriate for the size of container, tanks and tank cars or 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 drums in accordance with 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 *EDTA, Standard Solution* (0.01 *M*)—Transfer 40.0 mL of this solution from a buret into a 250-mL assay beaker or wide-mouthed flask. Add 50 mL of isopropyl alcohol, 10 mL of buffer solution, and 0.2 g of indicator (6.7). Mix thoroughly by swirling. Titrate with standard $ZnCl_2$ solution (6.9) to the first permanent tinge of red. Calculate the exact molarity of this approximately 0.01 *M* solution as follows:

$$M_1 = V_2M_2/V_1 \quad (2)$$

where:
M_1 = molarity of EDTA solution,
V_2 = $ZnCl_2$ solution, mL,
M_2 = molarity of $ZnCl_2$ solution, and
V_1 = 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 medicine dropper) and obtain the total weight. Weigh by difference to 0.5 mg, 0.18 to 0.22-g specimens (8 to 12 drops), into 400-mL beakers. This specimen size is for driers of 6 % iron content; adjust the size according to expected percent iron to contain about 0.2 mM of iron. Add 100 mL of isopropyl alcohol and 3 mL 1 + 3 HCl to each specimen and swirl to mix. Add a few boiling aids and heat the solution just to boiling on a hot plate; remove and cool to room temperature in a water bath.

9.3 From a buret measure 40.0 mL of standard EDTA solution into each beaker. Neutralize with dilute NH_4OH (1 + 3), as indicated by a change in the color of the solution from yellow to reddish. Add 10 mL of the buffer solution and 0.3 g of the Eriochrome Black-T indicator mixture. This addition should result in a blue-colored solution. Immediately back-titrate the excess EDTA with the standard $ZnCl_2$ solution (Note 3) to the first permanent tinge of red (Note 4). The back-titration must be completed within 2 min (Note 5 and Note 6).

NOTE 3—During the titration stir the solution manually or by means of a magnetic stirrer.

NOTE 4—To some observers, this color change appears as a change to purple. However, the transition is sharp and, with a little practice, easily noted.

NOTE 5—The time used in the titration step with $ZnCl_2$ solution affects the results. A titration time of less than 2 min gives consistently good results. Longer times give higher results.

NOTE 6—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 of iron present as follows:

$$\text{Iron, \%} = (V_3M_1 - V_4M_2)\ 5.59/S \quad (3)$$

where:
V_3 = EDTA solution, mL,
M_1 = molarity of EDTA solution,
V_4 = $ZnCl_2$ solution, required for specimen, mL,
M_2 = molarity of $ZnCl_2$ solution,
S = sample used, g, and
5.59 = millimolar weight of Fe × 100

11. Precision and Bias [6]

11.1 The precision estimates are based on an interlaboratory study in which one operator in seven different laboratories analyzed in duplicate on two different days two samples of iron drier containing 6 and 3 % iron. The 6 % iron drier was a commercially supplied sample and the 3% drier was obtained by quantitative dilution of the 6 % drier. The results were analyzed statistically in accordance with Practice E 180 and the within-laboratory coefficient of variation was found to be 0.26 % relative at 12 degrees of freedom and the between-laboratories coefficient of variation was 1.46 % relative at 10 degrees of freedom. 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 0.8 % 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 4.6 % relative.

[6] Supporting data are available from ASTM International Headquarters. Request RR: D01-1021.

11.2 *Bias*—Bias cannot be determined because there is no accepted standard for iron in paint driers.

12. Keywords

12.1 EDTA methods; driers; iron driers; paint driers