Designation: D3970 – 05 (Reapproved 2017)

Standard Test Method for
Cerium in Paint Driers by Oxidimetric Determination[1]

This standard is issued under the fixed designation D3970; 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 cerium in liquid cerium and rare earth paint driers and utilizes ferrous ammonium sulfate.

1.2 This test method is not applicable to dryer blends.

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

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.* For a specific hazard statement, see Section 7.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D444 Test Methods for Chemical Analysis of Zinc Yellow Pigment (Zinc Chromate Yellow)
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Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]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 organic constituents of the liquid drier specimen are eliminated by treatment with nitric, sulfuric, and hydrochloric acids, and the cerium is converted to cerous sulfate. The cerous sulfate is oxidized to ceric sulfate with sodium bismuthate and titrated with standard ferrous ammonium sulfate.

4. Significance and Use

4.1 This test method may be used to confirm in the presence of rare earths the stated cerium content of liquid pure cerium or rare earth driers manufactured for use in the coatings industry.

5. Interferences

5.1 This test method is specific for cerium in the presence of rare earth metals. Other drier metals with more than one valence may interfere and should be absent.

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 purchased or prepared 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.

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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.

6.3 *Ceric Sulfate Solution, Standard* (0.1 *N*)—Standardized 0.1 *N* solutions of ceric sulfate ($Ce(SO_4)_2$) in 1 *N* sulfuric acid may be purchased or prepared.[5]

6.4 *Ferroin Indicator* (0.025 *M*)—Orthophenanthroline ferrous complex indicator.[6]

6.5 *Ferrous Ammonium Sulfate Solution, Standard* (0.1 *M*)—Standardized ferrous ammonium sulfate ($FeSO_4 \cdot (NH_4)_2SO_4$), 0.1 *M*, may be purchased or prepared in the following manner. Dissolve 39.2 g of ferrous ammonium sulfate in 250 mL of distilled water and add 20 mL of concentrated sulfuric acid with stirring. Dilute to 1 L in a volumetric flask and standardize as follows:

6.5.1 Pipet duplicate 20.0-mL portions of standard 0.1 *N* ceric sulfate solution into 400-mL beakers and add 200-mL of 1.5 *N* sulfuric acid. Titrate with 0.1 *N* ferrous ammonium sulfate solution as described in 6.6. Calculate the molarity, *M*, of this approximately 0.1 *M* solution as follows:

$$M = V_2 N / V_1 \quad (1)$$

where:

V_2 = ceric sulfate solution, mL,
N = normality of ceric sulfate solution, and
V_1 = ferrous ammonium sulfate solution, mL.

6.6 *Ferrous Ammonium Sulfate Solution, Standard* (0.01 *M*)—Transfer 100 mL of the standardized 0.1 *M* ferrous ammonium sulfate solution from a volumetric flask to a 1-L volumetric flask and dilute with distilled water. This 0.01 *M* ferrous ammonium sulfate solution is designated as M_2. Alternatively, 0.2 *N* ferrous ammonium sulfate solution (see Test Methods D444) may be used and diluted to 0.01 *M* in accordance with 6.5.

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

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

6.9 *Sodium Bismuthate ($NaBiO_3$)*[7]—The grade required is a yellow powdery solid. If it is any other color it has decomposed and fresh material should be obtained.

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

6.11 *Sulfuric Acid (1 + 49, 2 %)*—Dilute 10 mL of the concentrated sulfuric acid (H_2SO_4) to 500 mL with water.

6.12 *Sulfuric Acid* (1.5 *N*)—Dilute 16.7 mL of concentrated sulfuric acid (H_2SO_4) to 400 mL with water.

7. Precautions

7.1 Use only a rubber bulb aspirator for pipetting liquids.

8. Sampling

8.1 Take a small sample of liquid drier from bulk using the procedures in Practice E300 appropriate for the size of container: Bottle Sampling section for tanks and tank cars or Tube Sampling section 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 the Tube Sampling section of Practice E300.

8.2 Examine the sample of drier for sediment or suspended matter which, if present, is evidence of noncompliance with the Physical Appearance requirements section of Specification D600.

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

9. Procedure

9.1 For the analysis use 1.0 g for 6 % of cerium and 2.0 g or more for materials containing proportionally less cerium. Rare earth driers are generally 45 to 50 % cerium. Thus in the analysis of 6 % rare earth driers, containing cerium, use 2.0 g. Weigh the specimen from a weighing bottle or syringe by difference, to 0.5 mg, transferring the specimen to a 250-mL Erlenmeyer flask.

9.2 Place the flask on a hot plate and warm to volatilize solvent (Note 2). Cool the flask.

NOTE 2—It is easier to volatilize the solvent than to destroy it with acid.

9.3 Under a hood, add 10 mL of HNO_3 and 10 mL of HCl to the specimen in the flask. Add boiling aids, heat strongly on a hot plate, and boil down to 2 to 3 mL. Repeat the acid addition and boiling down.

NOTE 3—Sulfuric acid is not added at the beginning of the digestion because it carbonizes the material making it more difficult to digest.

9.4 Add 10 mL of concentrated H_2SO_4 (Note 3), and 10 mL of HNO_3, and heat strongly on the hot plate until the evolution of brown fumes ceases and white fumes appear. At this point salt precipitation causes a tendency to bump which may be avoided by mixing while heating until the salt dissolves. Cool. All HCl must be removed before proceeding to 9.5. If thick fumes appear the HCl has been removed.

9.5 Add 100 mL of 2 % H_2SO_4, and 1.0 g of $NaBiO_3$, and bring to a boil. Cool.

9.6 Vacuum filter through a medium fritted-glass filter, rinse flask and filter with 2 % H_2SO_4, and wash the filter with an additional 150 mL of 2 % H_2SO_4. The filter may be used for several determinations without cleaning. When it plugs, it can be cleaned easily with HCl.

9.7 Dilute the solution to approximately 400 mL with water and titrate with 0.01 *M* ferrous ammonium sulfate until the

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[5] The sole source of supply of reagent grade 0.1 *N* solution of ceric sulfate in 1 *N* sulfuric acid, known to the committee at this time is G. Frederick Smith Co. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[6] The sole source of supply of 0.025 *M* ferroin indicator, known to the committee at this time is G. Frederick Smith Co. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[7] The sole source of supply of reagent grade sodium bismuthate, known to the committee at this time is Mallinckrodt Co. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

yellow color is barely perceptible. Add 1 drop of 0.025 *M* orthophenanthroline ferrous complex indicator and complete the titration. The color change is from clear to orange.

10. Calculation

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

$$A = \frac{V_3 M_2 (14.0)}{S} \quad (2)$$

where:

V_3 = ferrous ammonium sulfate solution, mL,
M_2 = molarity of ferrous ammonium sulfate solution,
14.0 = millimolar weight of cerium × 100, and
S = weight of specimen used, g.

11. Precision[8]

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 samples of cerium and rare earth driers containing 6 and 3 % cerium. Both were commercially supplied drier solutions. The results were analyzed statistically in accordance with Practice E180 and after deletion of one laboratory's results the within-laboratory coefficient of variation was found to be 0.75 % relative at 12 df and the between-laboratory coefficient of variation was 2.63 % relative at 10 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 2.3 % 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 8.3 % relative.

12. Bias

12.1 Bias cannot be determined for this method because there are no accepted standards for cerium in paint driers.

13. Keywords

13.1 cerium drier; drier analysis; ferrous ammonium sulfate; paint driers; rare earth driers

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[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1032. Contact ASTM Customer Service at service@astm.org.