



Designation: D 1394 – 76 (Reapproved 1999)

## Standard Test Methods for Chemical Analysis of White Titanium Pigments<sup>1</sup>

This standard is issued under the fixed designation D 1394; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 These test methods cover procedures for the chemical analysis of white titanium dioxide pigments.

1.2 The analytical procedures appear in the following order:

	Sections
Preparation of Sample	4
Qualitative Analysis	5 and 6
Moisture	7
Total Titanium:	
Jones Reductor Method	8-12
Aluminum Reduction Method	13-17
Aluminum Oxide	18-22
Silica	23-29

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. A specific hazard statement is given in Section 19.*

### 2. Referenced Documents

2.1 *ASTM Standards:*

D 280 Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>4</sup>

### 3. Reagents

3.1 *Purity of Reagent*—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.<sup>5</sup> 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type IV of Specification D 1193.

### 4. Preparation of Sample

4.1 The sample shall, in all cases, be thoroughly mixed and comminuted before taking portions for analysis.

### QUALITATIVE ANALYSIS

#### 5. Reagents

5.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

5.2 *Ammonium Sulfate*—( $(\text{NH}_4)_2\text{SO}_4$ ).

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

5.4 *Hydrogen Peroxide* (30 %)—Concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

5.5 *Hydrogen Sulfide* ( $\text{H}_2\text{S}$ ).

5.6 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

5.7 *Sulfuric Acid* (1+19)—Carefully mix 1 volume of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) with 19 volumes of water.

5.8 *Tartaric Acid*.

5.9 *Tin or Zinc Metal*.

#### 6. Procedure

6.1 Place about 0.5 g of the sample in a 250-mL glass beaker,<sup>6</sup> and add 20 mL of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) and 7 to 8 g of  $(\text{NH}_4)_2\text{SO}_4$ . Mix well and boil for a few minutes. The sample should go completely into solution; a residue denotes the presence of silicon dioxide ( $\text{SiO}_2$ ) or siliceous matter. Cool the solution, dilute with 100 mL of water, heat to boiling, let settle, filter, wash with hot  $\text{H}_2\text{SO}_4$  (1+19) until free of titanium, and

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-1 on Paints and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>5</sup> *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.

<sup>6</sup> Borosilicate glass has been found satisfactory for this purpose.

test the residue for lead, etc.

6.2 Test the filtrate for calcium, zinc, iron, chromium, etc., by the regular methods of qualitative analysis.<sup>7</sup> For the iron determination add to a portion of the filtrate 5 g of tartaric acid, render slightly ammoniacal, pass in H<sub>2</sub>S in excess, and digest on a steam bath. No precipitate after 30 min indicates the absence of iron, nickel, cobalt, lead, copper, etc. A black precipitate readily soluble in dilute HCl denotes iron. For titanium, test a small portion of the original filtrate with H<sub>2</sub>O<sub>2</sub> (a clear yellow-orange color should result) and another portion with metallic tin or zinc (a pale blue to violet coloration should result). Negative results should be shown for sulfide, carbonate, or appreciable water-soluble matter.

## MOISTURE

### 7. Procedure

7.1 Determine moisture and other volatile matter in accordance with Test Method A of Test Methods D 280.

## TOTAL TITANIUM BY THE JONES REDUCTOR METHOD

### 8. Scope

8.1 This method gives results similar to those obtained with the Aluminum Reduction Method, Sections 13-17.

### 9. Apparatus

9.1 *Jones Reductor*<sup>8</sup> having a zinc column at least 450 mm in length, and 19 mm in diameter (Fig. 1 and Fig. 2). The filtering pad must be tight enough to hold all the particles of amalgamated zinc resting on it, and may be made of asbestos or, preferably, glass-wool supported by platinum gauze or a perforated porcelain plate. Use the least amount (0.1 to 1.0 %) of mercury that will enable satisfactory control of hydrogen evolution, since heavy amalgamation tends to reduce the rate of reaction. Prepare the amalgam by washing 20-mesh zinc for 1 min in enough 1 N HCl to cover it, adding the proper amount of 0.25 M mercuric nitrate or chloride solution, and stirring rapidly for 3 min. Decant the solution and wash the amalgam with water and store under water to which a few drops of HCl have been added. After using, keep the reductor filled with water when not in use, in order that basic salts will not be formed and clog it.

### 10. Reagents

10.1 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH<sub>4</sub>OH).

10.2 *Ammonium Sulfate* ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>).

10.3 *Carbon Steel or Iron*—Pure iron or plain carbon steel.

10.4 *Ferric Sulfate Solution* (1 mL = 0.02 g Fe)—Dissolve 20 g of iron or carbon steel in a slight excess of HCl, oxidize with approximately 12 mL of HNO<sub>3</sub>, add about 80 mL of

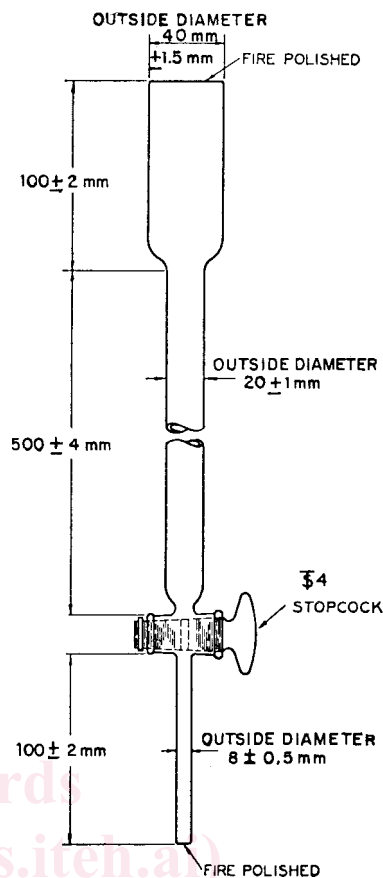


FIG. 1 Jones Reduction

H<sub>2</sub>SO<sub>4</sub>, and heat to dense white fumes. Cool, dilute with water to 1 L, digest on a steam bath until sulfates are dissolved, and filter if necessary. To oxidize any ferrous iron that may be present, add 0.1 N KMnO<sub>4</sub> solution until a faint pink color persists for 5 min. Ferric ammonium sulfate (FeNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O) may also be used to prepare this solution (See 15.4).

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

10.6 *Iron or Carbon Steel*—Pure iron or plain carbon steel.

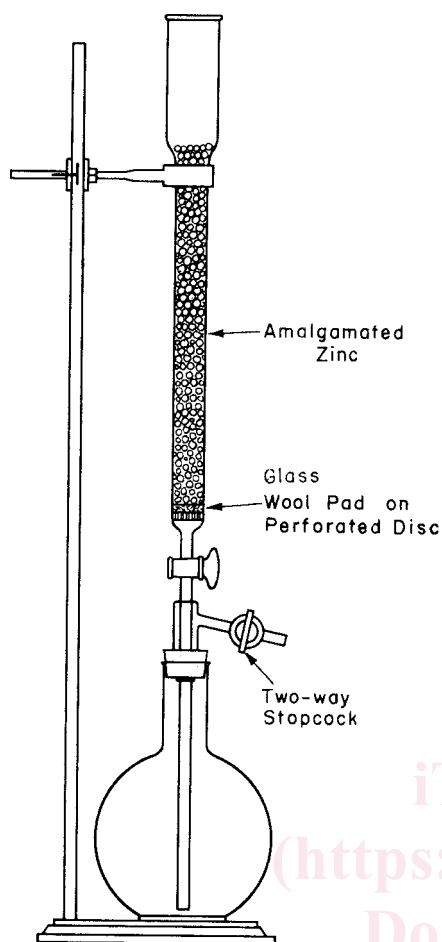
10.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

10.8 *Sodium Oxalate*—National Institute of Standards and Technology standard reference material No. 40 of sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>).

10.9 *Potassium Permanganate, Standard Reference Material* (0.1 N, 1 mL = 0.008 g TiO<sub>2</sub>)—Dissolve 3.16 g of KMnO<sub>4</sub> in water and dilute to 1 L. Let stand 8 to 14 days, siphon off the clear solution (or filter through sintered glass, medium porosity), and standardize against the National Bureau of Standards standard sample No. 40 of sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) as follows: In a 400-mL beaker dissolve 250 to 300 mg Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in 250 mL of hot water (80 to 90°C) and add 15 mL of H<sub>2</sub>SO<sub>4</sub> (1+1). Titrate at once with the KMnO<sub>4</sub> solution, *stirring the liquid vigorously and continuously*. The KMnO<sub>4</sub> solution must not be added more rapidly than 10 to 15 mL/min, and the last 0.5 to 1 mL must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution shall not be below 60°C by the time

<sup>7</sup> Treadwell, F. P., and Hall, William T., *Qualitative Analysis*, John Wiley & Sons, Inc., New York, NY, Vol. 1, Ninth English Ed., 1937.

<sup>8</sup> Directions for preparing a Jones Reductor may be found in Hillebrand, W. F., et al., *Applied Inorganic Analysis*, John Wiley & Sons, Inc., New York, NY, Second Ed., 1953, p. 108.



**FIG. 2 Jones Reductor, Assembled**

weigh as rapidly as possible. Calculate the dry weight of the specimen and use in the actual calculation.

11.3 Transfer the dried specimen to a dry 250 mL chemical- and heat-resistant glass beaker,<sup>6</sup> add 20 mL of H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) and 7 to 8 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Mix well and heat on a hot plate until dense white fumes are evolved, and then continue the heating over a strong flame until solution is complete (usually requires not over 5 min of boiling) or it is apparent that the residue is composed of SiO<sub>2</sub> or siliceous matter. Caution should be observed in visually examining this hot solution. Cool the solution, dilute with 100 mL of water, stir, heat carefully to boiling while stirring, let settle, filter through paper, and transfer the precipitate completely to the paper.

11.4 Wash the insoluble residue with cold H<sub>2</sub>SO<sub>4</sub> (1+19) until titanium is removed. Dilute the filtrate to 200 mL and add about 5 mL of NH<sub>4</sub>OH to lower the acidity to approximately 10 to 15 % H<sub>2</sub>SO<sub>4</sub> (by volume). Wash out the Jones reductor with H<sub>2</sub>SO<sub>4</sub> (1+19) and water, leaving sufficient water in the reductor to fill to the upper level of the zinc. (These washings should require not more than one or two drops of 0.1 N KMnO<sub>4</sub> solution to obtain a pink color.) Empty the receiver, and put in it 25 mL of ferric sulfate solution. Reduce the prepared titanium solution as follows:

11.4.1 Run 50 mL of H<sub>2</sub>SO<sub>4</sub> (1+19) through the reductor at such a uniform rate as to require 5 to 10 min for passage.

11.4.2 Follow this with the titanium solution at such a uniform rate as to require 10 min to pass through the reductor.

11.4.3 Wash out with 100 mL of H<sub>2</sub>SO<sub>4</sub> (1+19).

11.4.4 Finally run through about 100 mL of water. Take care that the reductor is always filled with solution or water to the upper level of the zinc.

11.5 Gradually release the suction, wash thoroughly the glass tube that was immersed in the ferric sulfate solution, remove the receiver, and titrate immediately with 0.1 N KMnO<sub>4</sub> solution. Run a blank determination, using the same reagents and washing the reductor as in the above determination.

## 12. Calculation

12.1 Calculate the percent of TiO<sub>2</sub> as follows:

$$\text{TiO}_2, \% = \frac{(V_1 - B) \times T}{S} \times 100$$

where:

$V_1$  = KMnO<sub>4</sub> solution required for titration of specimen, mL

$B$  = KMnO<sub>4</sub> solution required for titration of the blank, mL

$T$  = TiO<sub>2</sub> equivalent of the KMnO<sub>4</sub> solution, g/mL, and

$S$  = dried specimen, g.

12.2 The results calculated in accordance with 12.1 will include iron, chromium, arsenic, and any other substance that is reduced by zinc and acid. However, appreciable quantities of interfering materials are not likely to be encountered in normal, white titanium pigments.

## TOTAL TITANIUM BY THE ALUMINUM REDUCTION METHOD

## 13. Scope

13.1 This method gives results similar to those obtained

the end point has been reached. (More rapid cooling may be prevented by allowing the beaker to stand on a small hot plate during the titration. The use of a small type thermometer as a stirring rod is most convenient.) Keep the KMnO<sub>4</sub> solution in a glass-stoppered bottle painted black to keep out light or in a brown glass bottle stored in a dark place. Calculate the TiO<sub>2</sub> equivalent in grams of TiO<sub>2</sub> per millilitre of the KMnO<sub>4</sub> solution as follows:

$$\text{TiO}_2 \text{ equivalent} = (W \times 1.192)/V$$

where:

$W$  = Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> used, g, and

$V$  = KMnO<sub>4</sub> solution required for the titration, mL.

10.10 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

10.11 *Sulfuric Acid* (1+1)—Carefully mix 1 volume of H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) into 1 volume of water with rapid stirring.

10.12 *Sulfuric Acid* (1+19)—Carefully mix 1 volume of H<sub>2</sub>SO<sub>4</sub> into 19 volumes of water with rapid stirring.

## 11. Procedure

11.1 Determine the dry weight of a weighing bottle and cap to 0.1 mg. Weight to 0.1 mg 300 to 350 mg of the sample to be analyzed into the weighing bottle.

11.2 Dry the specimen in the opened weighing bottle for 2 h at 105 to 110°C. Cool in a desiccator, cap the bottle, and