



Designation: D1394 – 76 (Reapproved 2020)

Standard Test Methods for Chemical Analysis of White Titanium Pigments¹

This standard is issued under the fixed designation D1394; 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.

This standard has been approved for use by agencies of the U.S. 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. A specific hazard statement is given in Section 19.*

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

[D280 Test Methods for Hygroscopic Moisture \(and Other Matter Volatile Under the Test Conditions\) in Pigments](#)

[D1193 Specification for Reagent Water](#)

¹ These test methods are under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.31 on Pigment Specifications.

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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.

[E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials](#)

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.³ 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 [D1193](#).

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 (NH₄OH).

5.2 *Ammonium Sulfate*—((NH₄)₂SO₄).

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

5.4 *Hydrogen Peroxide (30 %)*—Concentrated hydrogen peroxide (H₂O₂).

5.5 *Hydrogen Sulfide (H₂S)*.

5.6 *Sulfuric Acid (sp gr 1.84)*—Concentrated sulfuric acid (H₂SO₄).

³ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

5.7 *Sulfuric Acid (1+19)*—Carefully mix 1 volume of H_2SO_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,⁴ and add 20 mL of H_2SO_4 (sp gr 1.84) and 7 to 8 g of $(NH_4)_2SO_4$. Mix well and boil for a few minutes. The sample should go completely into solution; a residue denotes the presence of silicon dioxide (SiO_2) or siliceous matter. Cool the solution, dilute with 100 mL of water, heat to boiling, let settle, filter, wash with hot H_2SO_4 (1+19) until free of titanium, and test the residue for lead, etc.

6.2 Test the filtrate for calcium, zinc, iron, chromium, etc., by the regular methods of qualitative analysis.⁵ For the iron determination add to a portion of the filtrate 5 g of tartaric acid, render slightly ammoniacal, pass in H_2S 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_2O_2 (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 D280.

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*⁶ 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

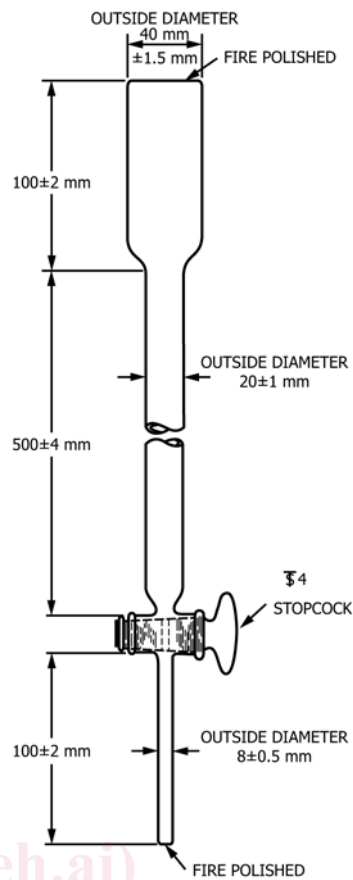


FIG. 1 Jones Reductor

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_4OH).

10.2 *Ammonium Sulfate* ($(NH_4)_2SO_4$).

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_3 , add about 80 mL of H_2SO_4 , 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 $KMnO_4$ solution until a faint pink color persists for 5 min. Ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) 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.

⁴ Borosilicate glass has been found satisfactory for this purpose.

⁵ Treadwell, F. P., and Hall, William T., *Qualitative Analysis*, John Wiley & Sons, Inc., New York, NY, Vol. 1, Ninth English Ed., 1937.

⁶ 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.

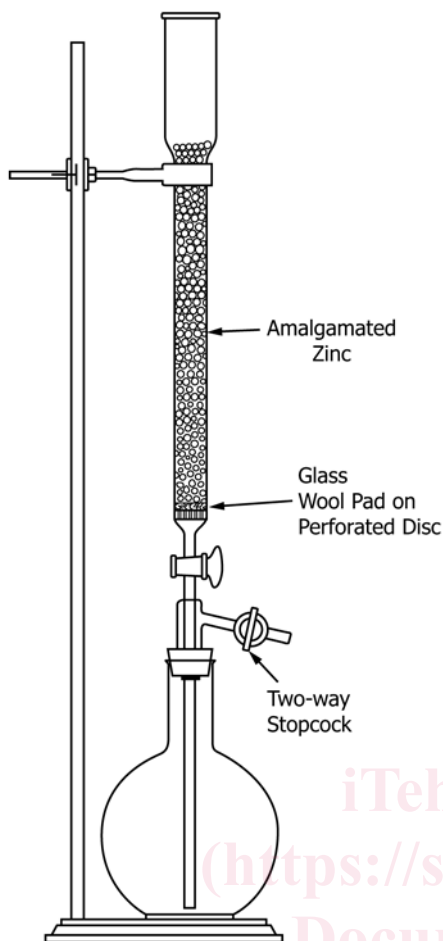


FIG. 2 Jones Reductor, Assembled

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

10.8 *Sodium Oxalate*—National Institute of Standards and Technology standard reference material No. 40 of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$).

10.9 *Potassium Permanganate, Standard Reference Material (0.1 N, 1 mL = 0.008 g TiO_2)*—Dissolve 3.16 g of KMnO_4 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 ($\text{Na}_2\text{C}_2\text{O}_4$) as follows: In a 400-mL beaker dissolve 250 to 300 mg $\text{Na}_2\text{C}_2\text{O}_4$ in 250 mL of hot water (80 to 90°C) and add 15 mL of $\text{H}_2\text{SO}_4(1+1)$. Titrate at once with the KMnO_4 solution, stirring the liquid vigorously and continuously. The KMnO_4 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 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_4 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_2 equivalent in grams of TiO_2 per millilitre of the KMnO_4 solution as follows:

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

where:

W = $\text{Na}_2\text{C}_2\text{O}_4$ used, g, and

V = KMnO_4 solution required for the titration, mL.

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

10.11 *Sulfuric Acid (1+1)*—Carefully mix 1 volume of H_2SO_4 (sp gr 1.84) into 1 volume of water with rapid stirring.

10.12 *Sulfuric Acid (1+19)*—Carefully mix 1 volume of H_2SO_4 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 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,⁴ add 20 mL of $\text{H}_2\text{SO}_4(\text{sp gr } 1.84)$ and 7 to 8 g of $(\text{NH}_4)_2\text{SO}_4$. 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_2 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 $\text{H}_2\text{SO}_4(1+19)$ until titanium is removed. Dilute the filtrate to 200 mL and add about 5 mL of NH_4OH to lower the acidity to approximately 10 to 15 % H_2SO_4 (by volume). Wash out the Jones reductor with $\text{H}_2\text{SO}_4(1+19)$ 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_4 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 $\text{H}_2\text{SO}_4(1+19)$ 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 $\text{H}_2\text{SO}_4(1+19)$.

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

KMnO₄ 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 TiO₂ as follows:

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

where:

V_1 = KMnO₄ solution required for titration of specimen, mL
 B = KMnO₄ solution required for titration of the blank, mL
 T = TiO₂ equivalent of the KMnO₄ 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 with the Jones Reductor Method (Sections 8 – 12).

14. Apparatus

14.1 *Delivery Tube*, made of about 4-mm inside diameter glass tubing bent so that there is a horizontal run of about 6 in. (152 mm) and a vertical drop of about 3 in. (76 mm) at one end, and a vertical drop of about 6 in. at the other end.

14.2 *Weighing Bottle*, wide-mouth, with an external-fitting cap, and no larger than necessary for the required amount of sample.

15. Reagents

15.1 *Aluminum Metal Foil*, electrolytic grade.

15.2 *Ammonium Sulfate*—((NH₄)₂SO₄).

15.3 *Ammonium Thiocyanate Indicator Solution*—Dissolve 24.5 g of ammonium thiocyanate (NH₄CNS) in 80 mL of hot water, filter, bring to room temperature, and dilute to 100 mL. Keep in a well-stoppered, dark-colored bottle.

15.4 *Ferric Ammonium Sulfate Solution* (1 mL = 0.005 g TiO₂)—Dissolve 30.16 g of fresh ferric ammonium sulfate (FeNH₄(SO₄)₂ · 12H₂O) in 800 mL of water containing 15 mL of H₂SO₄ (sp gr 1.84). Add 5 mL of 3 % H₂O₂ and boil for at least 15 min then cool to room temperature. Dilute to exactly 1 L and mix well. Filter if cloudy. Standardize using 190 to 210 mg of NBS standard reference material No. 154 of titanium dioxide and proceeding as directed in Section 16. Calculate the TiO₂ equivalent of the solution in grams of TiO₂ per millilitre of solution, as follows:

$$\text{TiO}_2 \text{ equivalent} = (W_1 \times P)/(V_2 \times 100)$$

where:

W_1 = National Bureau of Standards standard sample of TiO₂ used, g,
 P = percent TiO₂ in National Bureau of Standards standard sample, and
 V_2 = ferric ammonium sulfate solution required for the titration, mL.

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

15.6 *Hydrogen Peroxide*—3 %.

15.7 *Sodium Bicarbonate Solution*—Make up a saturated solution at the time of analysis. About 10 g of sodium bicarbonate (NaHCO₃) to 90 g of water is required.

15.8 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H₂SO₄).

15.9 *Titanium Dioxide* (TiO₂)—National Bureau of Standards standard sample No. 154 of titanium dioxide.

16. Procedure

16.1 Determine the dry weight of the weighing bottle and cap. Weigh to the nearest 0.1 mg, 190 to 210 mg of the sample to be analyzed into the weighing bottle.

16.2 Dry the specimen in the open weighing bottle for 2 h at 105 to 110°C. Cool in a desiccator, cap the bottle, and weigh as rapidly as possible. Calculate the dry weight of the specimen and use in the actual calculation.

16.3 Transfer the dry specimen to a 500-mL dry, wide-mouth Erlenmeyer flask. Add 7 to 9 g of (NH₄)₂SO₄ and 20 mL of H₂SO₄. Mix well, heat on a hot plate until dense white fumes are evolved, and 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 SiO₂ or siliceous matter. Cool and, with caution, add 120 mL of water and 20 mL of HCl. Bring to a boil and remove from heat.

16.4 Insert the short end of the delivery tube into one hole of a two-hole rubber stopper suitable for the Erlenmeyer flask. Insert a glass rod with a slight hook or collar at the bottom end into the other hole of the stopper in such a way that the bottom end will be near the bottom of the flask when the stopper is inserted into the flask. Attach approximately 1 g of aluminum foil to the bottom end of the rod by crumpling or coiling the foil around the rod. It may be possible to use a thermometer instead of a collared glass rod and, if one ranging from 0 to 150°C is used, it can be used for determining temperature later. Insert the stopper, carrying the rod with the foil and the delivery tube, into the flask in such a way that the foil will be near the bottom of the flask at the same time that the long end of the delivery tube will be near the bottom of a 250-mL beaker containing about 150 mL of NaHCO₃ solution.

16.5 As soon as dissolution of the aluminum is complete, heat the flask to gentle boiling for 3 to 5 min without removing the delivery tube from the NaHCO₃ solution. Cool to about 60°C, preferably by partial immersion of the flask in a vessel of water. The NaHCO₃ solution should siphon into the flask