Designation: D1394 – 76 (Reapproved 2014)

Standard Test Methods for Chemical Analysis of White Titanium Pigments[1]

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 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:*[2]

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

D1193 Specification for Reagent Water

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 (NH_4OH).

5.2 *Ammonium Sulfate*—($(NH_4)_2SO_4$).

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

5.4 *Hydrogen Peroxide (30 %)*—Concentrated hydrogen peroxide (H_2O_2).

5.5 *Hydrogen Sulfide* (H_2S).

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

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.*

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[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.

[3] *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. 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 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.

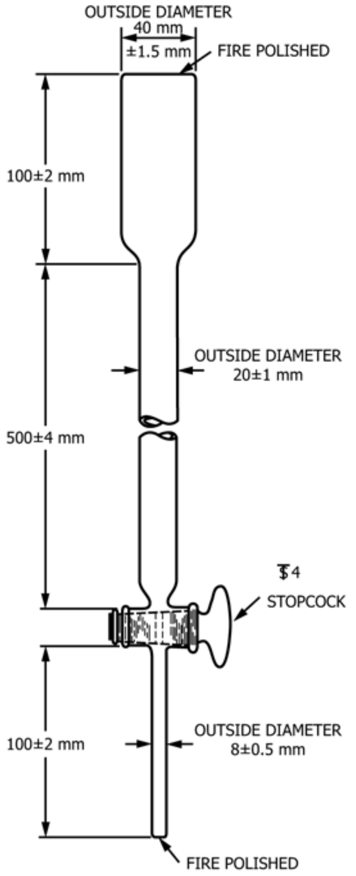

FIG. 1 Jones Reduction

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.

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 ($Na_2C_2O_4$).

10.9 *Potassium Permanganate, Standard Reference Material* (0.1 *N*, 1 mL = 0.008 g TiO_2)—Dissolve 3.16 g of $KMnO_4$

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[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.

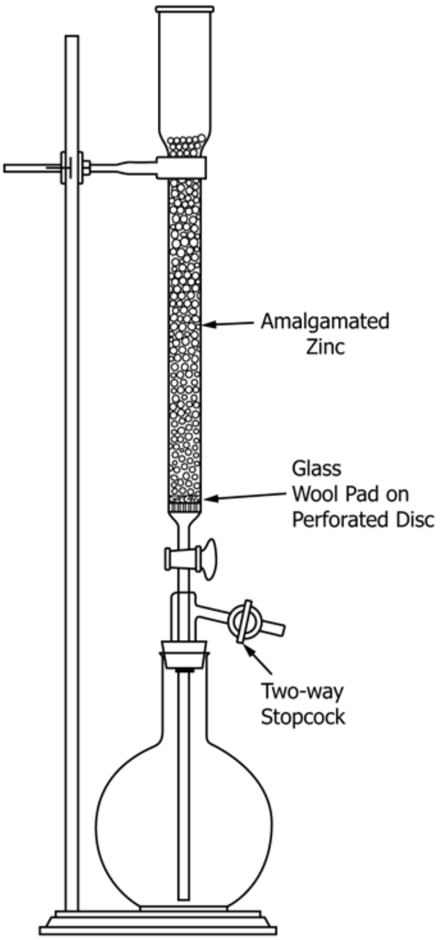

FIG. 2 Jones Reductor, Assembled

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 ($Na_2C_2O_4$) as follows: In a 400-mL beaker dissolve 250 to 300 mg $Na_2C_2O_4$ in 250 mL of hot water (80 to 90°C) and add 15 mL of H_2SO_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:

$$\mathrm{TiO_2\ equivalent} = (W \times 1.192)/V$$

where:

W = $Na_2C_2O_4$ 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 H_2SO_4(sp gr 1.84) and 7 to 8 g of $(NH_4)_2SO_4$. 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 H_2SO_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 H_2SO_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 H_2SO_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 H_2SO_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* $KMnO_4$ 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_2 as follows:

$$\mathrm{TiO_2},\ \% = \frac{(V_1 - B) \times T}{S} \times 100$$

where:

V_1 = $KMnO_4$ solution required for titration of specimen, mL
B = $KMnO_4$ solution required for titration of the blank, mL
T = TiO_2 equivalent of the $KMnO_4$ 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*—($(NH_4)_2SO_4$).

15.3 *Ammonium Thiocyanate Indicator Solution*—Dissolve 24.5 g of ammonium thiocyanate (NH_4CNS) 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 TiO_2)—Dissolve 30.16 g of fresh ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) in 800 mL of water containing 15 mL of H_2SO_4 (sp gr 1.84). Add 5 mL of 3 % H_2O_2 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 TiO_2 equivalent of the solution in grams of TiO_2 per millilitre of solution, as follows:

$$TiO_2 \text{ equivalent} = (W_1 \times P)/(V_2 \times 100)$$

where:

W_1 = National Bureau of Standards standard sample of TiO_2 used, g,
P = percent TiO_2 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 ($NaHCO_3$) to 90 g of water is required.

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

15.9 *Titanium Dioxide (TiO_2)*—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 $(NH_4)_2SO_4$ and 20 mL of H_2SO_4. 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 SiO_2 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 $NaHCO_3$ 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 $NaHCO_3$ solution. Cool to about 60°C, preferably by partial immersion of the flask in a vessel of water. The $NaHCO_3$ solution should siphon into the flask during this cooling, giving an atmosphere of CO_2 over the reduced titanium solution. Withdraw the stopper, but rinse the glass rod attached to it with a little water, catching the rinse water in the flask before removing the stopper, rod, and delivery tube completely.

16.6 Add 2 mL of NH_4CNS indicator solution and titrate immediately with ferric ammonium sulfate solution (15.4) to a straw-colored end point. It is best to add the bulk of the ferric ammonium sulfate solution at once, shake well, and finish the titration drop by drop.

17. Calculations

17.1 Calculate the percent of TiO_2 as follows:

$$TiO_2, \% = (V_3 \times T_1 \times 100)/S$$

where:

V_3 = ferric ammonium sulfate solution required for titration of specimen, mL,
T_1 = TiO_2 equivalent of the ferric ammonium sulfate solution, g/mL, and
S = dried specimen, g.

17.2 The results calculated in accordance with 17.1 will include chromium, arsenic, and any other substance which is reduced by aluminum and subsequently oxidized by ferric ion. However, appreciable quantities of interfering materials are not likely to be encountered in normal, white titanium pigments.

ALUMINUM OXIDE

18. Scope

18.1 This method covers the determination of aluminum oxide in titanium dioxide pigments.

19. Reagents

NOTE 1—**Precaution:** All solutions should be stored in polyethylene bottles.

19.1 *Acetic Acid,* glacial.

19.2 *Ammonium Acetate Solution (Buffer Solution)*—Dissolve 77 g of ammonium acetate in water, add 10 mL of glacial acetic acid and dilute with water to 1 L.

19.3 *Ammonium Hydroxide (1+4)*—Dilute 1 volume of concentrated ammonium hydroxide (sp gr 0.90) with 4 volumes of water.

19.4 *Ammonium Phosphate, Dibasic Solution*—Dissolve 150 g of $(NH_4)_2HPO_4$ in 700 mL of water. Adjust pH to 5.5 with HCl (1+1). Dilute with water to 1 L.

19.5 *EDTA Solution (0.02 M)*—Dissolve 7.45 g of disodium ethylenediamine tetraacetate dihydrate in water and dilute to 1 L.

19.6 *Hydrochloric Acid (1+1)*—Dilute 1 volume of concentrated hydrochloric acid (sp gr 1.19) with 1 volume of water.

19.7 *Methyl Orange Indicator Solution*—Dissolve 0.1 g of methyl orange in 100 mL of water, in accordance with Practices E50.

19.8 *Sodium Bisulfate Monohydrate*—($NaHSO_4 \cdot H_2O$).

19.9 *Sodium Fluoride* (NaF).

19.10 *Sodium Hydroxide Solution (6.25 M)*—Dissolve 500 g of sodium hydroxide (NaOH) in water and dilute to 2 L.

19.11 *Sulfuric Acid (1+1)*—To 1 volume of water add slowly with stirring 1 volume of concentrated H_2SO_4.

19.12 *Xylenol Orange Indicator Solution*—Dissolve 0.2 g of xylenol orange tetrasodium salt in 100 mL of water. Renew solutions weekly.

19.13 *Zinc Sulfate, Standard Solution(0.01 M)*—Dissolve 2.90 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 L. Standardize as follows:

19.13.1 Dissolve with the aid of heat 0.50 g of high-purity (99.8 %) aluminum wire, weighed to 0.1 mg, in 20 mL of concentrated HCl. Transfer to a 1-L volumetric flask and dilute to volume with water.

19.13.2 Place a 10-mL aliquot of this solution into a 500-mL Erlenmeyer flask containing approximately 90 mL of water and 3 mL of HCl. Add 1 drop of methyl orange indicator solution. Continue with step 20.4.

19.13.3 Calculate the titre of the $ZnSO_4$ solution as follows:

$$A = (18.8955 \times W_1)/V_4$$

where:

A = Al_2O_3 per millilitre of $ZnSO_4$ solution, mL,
W_1 = weight of aluminum wire dissolved in 19.13.2, g,
V_4 = $ZnSO_4$ solution consumed in the second titration, mL, and

$$18.8955 = \frac{\text{mol weight of } Al_2O_3 \times 10}{2 \times \text{mol weight of Al}}$$

20. Procedure

20.1 Fuse about 1 g of pigment weighed to 0.1 mg with 10 g of $NaHSO_4 \cdot H_2O$ in a 250-mL Erlenmeyer flask until the melt is clear. Use a 250-mL high-silica glass Erlenmeyer flask to prevent cracking. Do not use more sodium bisulfate than specified since excess concentrations of salt will interfere with the EDTA titration. Heat on a hot plate starting at low heat, then gradually raise the heat until full heat is reached. When the spattering has stopped and light fumes of SO_3 appear, heat the flask in the full flame of a Meker burner, with the flask tilted so that the fusion is concentrated at one end of the flask. Swirl constantly until the melt is clear. Avoid prolonged heating to prevent precipitation of titanium dioxide. Cool and add 25 mL of H_2SO_4(1+1). Heat until the mass has dissolved, and a clear solution results. (If silica is present, a little insoluble silica may remain.) Cool and add 120 mL of water.

20.2 Measure out 200 mL of 6.25 *M* NaOH solution. Add 65 mL of this NaOH solution to the sample solution while stirring constantly with a magnetic stirrer. Pour the remaining NaOH solution into a 500-mL volumetric flask. Slowly, and with constant stirring, add the sample solution to the NaOH solution. Police with water, cool, and dilute to volume. (If the procedure is delayed at this point for more than 2 h, transfer the contents of the volumetric flask to a polyethylene bottle.) Either centrifuge for 5 min, or allow most of the precipitate to settle out, then filter the supernatant liquid through a very fine filter paper until a little more than 100 mL have been collected.

20.3 Place a 100-mL aliquot of the above solution in a 500-mL Erlenmeyer flask, add 1 drop of methyl orange indicator solution and acidify with HCl (1+1) until the color changes to red; add approximately 3 mL in excess.

20.4 Add 25 mL of EDTA solution. (If the approximate alumina level is known, use the following mathematical formula for determining the amount of EDTA to add for best results: $4 \times \%\ Al_2O_3 + 5 = \text{mL of } 0.02\ M$ EDTA.) Add, dropwise, NH_4OH (1+4) until the solution color is just completely changed from red to orange-yellow. Add 10 mL of buffer solution and 10 mL of $(NH_4)_2 \cdot HPO_4$ solution, boil for 5 min, and cool quickly to room temperature in running water. Add 3 drops of xylenol orange indicator solution. If the solution is purple, yellow-brown, or pink, bring the pH to 5.3–5.7 with acetic acid. If the pH is correct, a pink color indicates insufficient EDTA; repeat with a new aliquot, starting with 20.3 and using 50 mL of EDTA solution in 20.4.

20.5 Titrate with $ZnSO_4$ solution to a yellow-brown or pink end point. This titration should be performed quickly near the end point by rapidly adding 0.2-mL increments until the first color change occurs. This color will fade in 5 or 10 s, but is the true end point. This step is critical, and failure to observe the first color change will result in an incorrect value. The fading end point does not occur in the second titration. This first titration must be greater than 8 mL of $ZnSO_4$ solution. For most accurate work this first titration should require 10 to 15 mL of $ZnSO_4$ solution.

20.6 Add 2 g of NaF, boil for 2 to 5 min, and cool in running water. Titrate the EDTA, released from its aluminum complex by the fluoride, with $ZnSO_4$ solution to the same end point as in 20.5.

21. Calculation

21.1 Calculate the aluminum oxide content of the pigment sample as follows:

$$A = (Z \times T)/(2 \times S) \tag{1}$$

where:

A = percent Al_2O_3,
Z = $ZnSO_4$ solution consumed in the second titration, mL,
T = Al_2O_3 per millilitre of $ZnSO_4$ solution, g, and
S = specimen used, g.

22. Precision

22.1 Based on interlaboratory studies the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

22.1.1 *Repeatability*—Two results obtained by the same operator on the same sample should be considered suspect if they differ by more than 0.22 % relative.

22.1.2 *Reproducibility*—Two results, each the mean of duplicates obtained by operators in different laboratories should be considered suspect if they differ by more than 0.62 % relative.

SILICA

23. Scope

23.1 This method covers the determination of silica in titanium dioxide (TiO_2) pigments.

24. Summary of Method

24.1 The fusion of TiO_2 pigment with sodium bisulfate leaves only the silica insoluble when the melt is dissolved in sulfuric acid. To assure no loss of the silica the sulfuric acid is taken to fuming to dehydrate the silica. The silica content is determined by volatilizing the silica in the weighed filtration residue with hydrofluoric acid.

25. Apparatus

25.1 *Erlenmeyer Flask,* 250-mL, high silica.

25.2 *Filter Paper,* very fine, ashless, acid washed.

25.3 *Platinum Crucible and Cover.*

25.4 *Oven,* controlled at 120°C.

25.5 *Muffle Furnace,* controlled at 1000 ± 25°C.

26. Reagents

26.1 *Hydrofluoric Acid (sp gr 1.15)*—Concentrated hydrofluoric acid (HF).

26.2 *Sodium Bisulfate*—($NaHSO_4 \cdot H_2O$).

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

26.4 *Sulfuric Acid (1+1)*—To 1 volume of water add slowly with stirring 1 volume of concentrated H_2SO_4.

26.5 *Sulfuric Acid (1+9)*—To 9 volumes of water add slowly with stirring 1 volume of concentrated H_2SO_4.

27. Procedure

27.1 Transfer 1 g of pigment weighed to 0.1 mg to a 250-mL high silica Erlenmeyer flask containing 10 g of $NaHSO_4 \cdot H_2O$. If an SiO_2 content in excess of 5 % is expected a 0.5-g specimen of pigment may be used to facilitate complete fusion with 10 g of $NaHSO_4 \cdot H_2O$.

27.2 Heat over a Meker burner, frequently swirling the flask until decomposition and fusion is complete and clear (except for SiO_2). *Be careful of overheating at start and of spattering of the fusion.*

27.3 Allow to cool and to the cold melt, add 25 mL of H_2SO_4(1+1), and heat very carefully and very slowly until the fusion is dissolved. Carefully evaporate to fumes of H_2SO_4.

27.4 Cool and carefully add 150 mL of water. Pour very small amounts of water down the sides of the flask with frequent swirling of the contents to avoid overheating and spattering. Let cool and filter through fine ashless filter paper, using a 60° gravity funnel.

27.5 Wash out all silica from the flask onto the filter paper with H_2SO_4(1+9). Police the flask carefully.

27.6 Place the filter paper in a platinum crucible and dry in a 120°C oven. Heat the partly covered crucible over a bunsen burner. Avoid flaming the filter paper by heating first the cover from above and then the crucible from below. When the filter paper is consumed, heat at 1000°C for 30 min in a muffle furnace. Cool in a desiccator and weigh the crucible.

27.7 Add 2 drops of H_2SO_4 (1+1) and 5 mL of HF (sp gr 1.15). Carefully evaporate to dryness, first on a low heat hot plate to remove the HF and then over a bunsen burner to remove the H_2SO_4. Avoid spattering, especially after removal of the HF.

27.8 Ignite at 1000°C for 10 min. Cool in a desiccator and weigh the crucible again. The difference in weight is silica.

28. Calculation

28.1 Calculate the silica content as follows:

$$SiO_2, \% = (W_2/S_3) \times 100$$

where:

W_2 = SiO_2 found, g, and
S_3 = specimen used, g.

29. Precision

29.1 On the basis of an interlaboratory test of this test method in which six laboratories tested, in duplicate, five samples of titanium dioxide ranging in silica content from 1.5 to 8.2 %, within-laboratory standard deviation was found to be 1.79 % and between-laboratories standard deviation was found to be 3.44 %. Based on this, the following criteria should be used for judging the precision of results at the 95 % confidence level:

29.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 5.1 % relative.

29.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 9.7 % relative.

30. Keywords

30.1 aluminum oxide; aluminum reduction; chemical analysis; Jones Reductor; titanium pigment

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