Designation: D4563 – 02 (Reapproved 2015)

Standard Test Method for Determination by Atomic Absorption Spectroscopy of Titanium Dioxide Content of Pigments Recovered From Whole Paint[1]

This standard is issued under the fixed designation D4563; 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 atomic absorption (AA) analysis of titanium dioxide content in pigments recovered from whole paint. It is applicable to quality control situations where the same type of product is repeatedly analyzed.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address 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.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1394 Test Methods for Chemical Analysis of White Titanium Pigments

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E288 Specification for Laboratory Glass Volumetric Flasks

3. Summary of Test Method

3.1 The specimen is prepared for analysis by ashing at 450°C followed by digestion with sulfuric acid and ammonium sulfate as in Test Methods D1394. The titanium content is determined by atomic absorption spectroscopy using a specimen similar to that previously analyzed by the Aluminum Reduction Method in Test Methods D1394.

3.2 By utilizing the pigment analyzed in Test Methods D1394 as an atomic absorption standard, several hundred TiO_2 determinations can be made. The AA technique is much faster than the technique in Test Methods D1394 for multiple determinations and uses only acids. This keeps reagents and time to a minimum.

4. Significance and Use

4.1 This test method may be used in quality control laboratories when the repeated analysis of titanium dioxide in similar paints may be required. Reagents and time are kept to a minimum when this test method is used in place of wet chemical analysis such as in Test Methods D1394. However, reproducibility and repeatability are not as good as in Test Methods D1394.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer,* consisting of

5.1.1 Atomizer and nitrous oxide burner,

5.1.2 Gas-pressure regulator and metering devices for nitrous oxide and acetylene,

5.1.3 Titanium hollow cathode lamp with regulated constant-current supply,

5.1.4 Monochromator and associated optics,

5.1.5 Photosensitive detector connected to an electronic amplifier,

5.1.6 Readout device.

5.2 *Muffle Furnace,* capable of maintaining 450 ± 25°C.

5.3 *Circulating Oven,* maintained at 105 ± 2°C.

5.4 *Porcelain Dishes,* 90-mm diameter.

5.5 *Plastic Disposable Syringe,* 10-mL capacity.

5.6 *Agate Mortar and Pestle,* 95-mm outside diameter.

5.7 *Wide-Mouth Erlenmeyer Flask,* 500-mL capacity.

5.8 *Hot Plate,* with variable surface temperature control from 10°C above ambient to 370°C accurate to within ±5°C.

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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.

5.9 *Burner.*

5.10 *Volumetric Flask,* 1000 mL, plastic (see Specification E288).

5.11 *Paint Shaker.*

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

5.13 *Desiccator.*

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.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without reducing 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.

6.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

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

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

6.6 *Hydrofluoric Acid (HF)*—Approximately 49 %.

6.7 *Standard Pigment Solution.*

6.7.1 Following the procedure in Section 9 recover the pigment from a paint that is similar to the unknown specimen. Analyze the extracted pigment for TiO_2 content in accordance with the Aluminum Reduction Method in Test Methods D1394 and record the percent TiO_2 found in the pigment.

6.7.2 Following the procedure in 12.1 – 12.5 take a specimen of the pigment extracted in 6.7.1 into solution. Store this solution for no more than 3 months in a plastic bottle marked with the percent TiO_2 as determined in 6.7.1.

6.8 *Sulfuric Acid* (sp gr 1.84), concentrated sulfuric acid (H_2SO_4).

6.9 *Toluene.*

7. Hazards

7.1 *Concentrated Hydrofluoric Acid*—Make certain to observe manufacturer's recommended precautions for handling.

7.2 **Warning—**Nitrous oxide and acetylene can cause explosions, if not used properly. See the supplier's manual of instructions for the atomic absorption instrument for proper operation with these gases.

8. Calibration and Standardization

8.1 Operational instructions for atomic absorption spectrophotometers vary with different models. Consult the manufacturer's literature for establishing optimum conditions for the specific instrument used.

8.2 Turn the instrument on and set the wavelength to the 365.3-nm titanium line. Apply the recommended current to the titanium hollow cathode lamp. Allow the instrument to warm up for about 15 min and set the proper slit width. Adjust the gas pressures and ignite the burner in accordance with instructions for using nitrous oxide and acetylene.

8.3 Aspirate the water to rinse the atomizer chamber from 10 to 15 min until the burner head achieves temperature equilibrium. Set the instrument reading to zero while doing this. While aspirating the working standard from 6.7.2 set the instrument to the percent TiO_2 (determined in 6.7.1). Reaspirate the water and reset the instrument to ZERO. Repeat this procedure until the readings become stable.

8.3.1 Expanding the scale of a spectrophotometer increases the noise level of the readout system. Therefore, if expanding the scale to make the readout indicate 60 % TiO_2 has this effect, do not use any expansion. For instance, it is not necessary to make the instrument read 60 for 60 % TiO_2 standard. It may read 30. If 60 % equals 30, a pigment giving a reading of 25 would have a TiO_2 content of 50 %.

PIGMENT CONTENT

9. Procedure

9.1 Mix the samples until homogenous, preferably on a mechanical shaker. If air bubbles become entrapped in the sample, stir by hand.

9.2 Draw approximately 5 g of the paint under test into a 10-mL syringe and weigh to 1 mg. Transfer, by dropwise addition, between 2.0 and 4.0 g of the specimen to a tared porcelain dish containing either 2 mL of water (for water-borne paint) or 2 mL of toluene (for solvent-borne paint). Reweigh the syringe to 1 mg. Swirl the dish during the addition of the paint and continue to swirl until the specimen is completely dispersed. If a water-borne paint tends to agglomerate or form lumps that cannot be dispersed, a drop or two of concentrated NH_4OH may help the dispersement. If the lumps persist, discard the specimen, and prepare a new one. Prepare a duplicate specimen in the same manner.

9.3 Dry the specimens at 110°C for 30 min and then drive off the remaining solvent or water at the lowest temperature possible using a Meker burner (under a hood). Do not leave the dishes on the burners after the flames have subsided.

9.4 Transfer the dried specimens to a muffle furnace and heat at 450 ± 25°C for at least 1 h and until no further char is evident. Leave the furnace door slightly open after first inserting the dishes to allow smoke and possibly flames to escape making certain the furnace is well vented.

9.5 Remove the dishes from the muffle furnace, cool in a desiccator, and weigh.

9.6 Grind the pigment to pass through an 80-mesh screen.

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[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.

10. Calculation

10.1 Calculate the percent pigment content as follows:

$$P = \frac{C - W_1}{W_2} \times 100 \tag{1}$$

where:

P = pigment content, %
C = weight of the dish and specimen after ignition, g,
W_1 = weight of the dish alone, g,
W_2 = specimen weight used, g.

11. Precision and Bias (see Practice E180)[5]

11.1 In an interlaboratory study of this test method in which operators in each of seven laboratories made duplicate analyses on different days and one operator in one laboratory made duplicate analyses on one day and a single analysis on the second day on a water-borne flat wall paint, a solvent-borne semi-gloss enamel and a solvent-borne house paint containing 33, 38.5, and 37 % pigment, respectively, the pooled within-laboratory standard deviation was found to be 0.07 % absolute with 21 df. The pooled between-laboratories standard deviation was 0.22 % absolute with 21 df. One laboratory's results for one day were discarded because the duplicates differed significantly and another laboratory's results for one day because the range differed significantly from all other ranges for Coating 1 and a third laboratory's results for one day because it differed significantly from the other day's results and those from all other laboratories for Coating 2. Based on these standard deviations 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 duplicates, obtained by the same operator should be considered suspect if they differ by more than 0.21 % absolute at pigment contents of 33 to 39 wt %.

11.1.2 *Reproducibility*—Two results, each the mean of duplicates obtained by operators in different laboratories, should be considered suspect if they differ by more than 0.66 % absolute at the same pigment content levels.

TITANIUM DIOXIDE CONTENT

12. Procedure

12.1 Determine the dry weight of two weighing bottles with caps. In accordance with Table 1 select the appropriate specimen weight and place the approximate amount of recovered pigment in each weighing bottle.

12.2 Dry the specimens in the open weighing bottles for 2 h at 105°C. Cool in a desiccator. After cooling, cap the weighing bottles and weigh as rapidly as possible.

12.3 Transfer the dry specimens to 500-mL wide-mouth Erlenmeyer flasks. Reweigh bottles and caps and record weights of specimens transferred (W_4 in equation in 13.1 and 13.2).

TABLE 1 Specimen Weight Requirement

Expected TiO_2 on pigment, %	Specimen Weight, mg[A]
0 to 19	1000
20 to 29	500
30 to 39	330
40 to 49	250
50 to 59	200
60 to 69	160
70 to 79	140
80 to 89	130
90 to 100	110

[A] Equivalent to about 60 ppm Ti in the final solution.

12.4 To the 500-mL flasks, which now contain the specimens, add 8 g ± 0.001 g of $(NH_4)_2SO_4$, 50 mL of concentrated H_2SO_4 and 5 drops of concentrated HNO_3. Mix well by swirling the flasks. Heat on a hot plate until dense white fumes are evolved. Continue heating over a hot flame until solutions are complete (usually requires not more than 5 min of boiling), or until it is apparent that the residues are composed of SiO_2 or siliceous matter. Cool and add 100 mL of water with extreme caution.

12.5 Quantitatively transfer the contents of the flasks including any insoluble matter to 1000-mL plastic volumetric flasks (see Specification E288). Add 50 mL of HCl and 30 mL of HF. Allow to cool to room temperature and then fill to the mark with water. Stopper and mix well. Transfer the solutions to plastic bottles (because of the HF) and store for no more than 3 months for analysis by AA. Solutions must be filtered through a Whatman 42 paper before being aspirated.

12.6 Calibrate the instrument in accordance with Section 8 and aspirate the solutions in the following order:

1—water (set to ZERO)
2—working standard (set to percent TiO_2)
3—specimen (read)
1—water (set to ZERO)
2—working standard (set to percent TiO_2)
3—specimen (read)

This MUST be repeated until the readings are stable.

13. Calculation

13.1 Calculate the percent TiO_2 in the pigment as follows:

$$TiO_2, \% = \frac{C \times W_3}{W_4} \tag{2}$$

where:

C = reading of specimen (number 3 in 12.6),
W_3 = standard pigment weight in 6.7.1, g, and
W_4 = specimen pigment weight in 12.3, g.

13.2 Calculate the percent TiO_2 in the whole paint as follows:

$$TiO_2\,\%, = \frac{P \times W_3 \times A}{W_4} \tag{3}$$

where:

A = pigment calculated in 10.1, %, and
P, W_3, and W_4 = same as in 13.1.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1046. Contact ASTM Customer Service at service@astm.org.

14. Precision and Bias (see Practice E180)[5]

14.1 In an interlaboratory study of this test method in which operators in each of eight laboratories analyzed on different days a water-borne flat wall paint, a solvent-borne semi-gloss enamel and a solvent-borne house paint, respectively containing 28.8, 56.8, and 42.8 weight % titanium dioxide in the pigment, the pooled within-laboratory standard deviation was found to be 0.65 % absolute with 22 degrees of freedom. The pooled between-laboratories standard deviation was 1.31 % absolute with 20 degrees of freedom. One duplicate value from one laboratory was discarded because the range differed significantly from all other duplicate ranges for Coating 1, one day's result from another laboratory because the range differed significantly from all other ranges and both day's results from a third laboratory were discarded because the mean differed significantly from all other laboratory means for Coating 2, and one duplicate value was discarded from the same laboratory as with Coating 1 because the range differed significantly from all other duplicate ranges for Coating 3. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

14.1.1 *Repeatability*—Two results, each the mean of duplicates obtained by the same operator, should be considered suspect if they differ by more than 1.91 % absolute at TiO_2 contents of 28 to 57 weight % of the pigment.

14.1.2 *Reproducibility*—Two results, each the mean of duplicates, obtained by operators in different laboratories should be considered suspect if they differ by more than 3.68 % absolute at the same levels of TiO_2 content.

14.2 *Bias*—Bias cannot be determined because there are no standards for titanium dioxide content of pigments recovered from whole paints.

15. Keywords

15.1 atomic adsorption spectroscopy; percent pigment by ignition; titanium dioxide; analysis of