



Designation: D 4563 – 02

Standard Test Method for Determination by Atomic Absorption Spectroscopy of Titanium Dioxide Content of Pigments Recovered From Whole Paint¹

This standard is issued under the fixed designation D 4563; 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 *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:

D 1193 Specification for Reagent Water²

D 1394 Test Methods for Chemical Analysis of White Titanium Pigments³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 288 Specification for Laboratory Glass Volumetric Flasks⁵

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 **D 1394**. 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 **D 1394**.

3.2 By utilizing the pigment analyzed in Test Methods **D 1394** as an atomic absorption standard, several hundred TiO₂

determinations can be made. The AA technique is much faster than the technique in Test Methods **D 1394** 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 **D 1394**. However, reproducibility and repeatability are not as good as in Test Methods **D 1394**.

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.

5.9 *Burner*.

5.10 *Volumetric Flask*, 1000 mL, plastic (see Specification **E 288**).

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.

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 *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.03.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ *Annual Book of ASTM Standards*, Vol 14.04.

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.⁶ 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 **D 1193**.

6.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH₄OH).

6.4 *Ammonium Sulfate (NH₄)₂SO₄*.

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 TiO₂ content in accordance with the Aluminum Reduction Method in Test Methods **D 1394** and record the percent TiO₂ 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 TiO₂ as determined in 6.7.1.

6.8 *Sulfuric Acid (sp gr 1.84)*, concentrated sulfuric acid (H₂SO₄).

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 TiO₂ (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 % TiO₂ has this effect, do not use any expansion. For instance, it is not necessary to make the instrument read 60 for 60 % TiO₂ standard. It may read 30. If 60 % equals 30, a pigment giving a reading of 25 would have a TiO₂ 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 NH₄OH 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.

10. Calculation

10.1 Calculate the percent pigment content as follows:

$$P = \frac{C - W_1}{W_2} \times 100 \quad (1)$$

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.

⁶ *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.