



Standard Test Methods for TITANIUM DIOXIDE IN PAPER¹

This Standard is issued under the fixed designation D 921; 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.

1. Scope

1.1 These methods cover the determination of titanium dioxide in paper. A qualitative method and two optional quantitative methods are given, as follows:

	Sections
Method A—Qualitative Test	6 and 7
Method B—Quantitative Determination by the Volumetric Method	8 to 12
Method C—Quantitative Determination by the Colorimetric Method	13 to 18

1.2 Method C is preferable when the amount of titanium dioxide in the ash is less than 0.01 g (Note 1). This method requires the use of a spectrophotometer or similar instrument for measuring light transmission.

NOTE 1—The presence of less than 0.01 g of titanium dioxide may be due to insufficient paper sample for volumetric analysis, or paper with a high filler content other than titanium dioxide, which is sometimes difficult to dissolve properly, due to bumping.

2. Significance

2.1 Since titanium dioxide is one of the most expensive mineral constituents used in paper, it is frequently desirable to know how much is present. This is particularly important when the pigment is used as a beater filler where there is always some question as to how much is actually being retained in the web. The method, therefore, has significance in control, in research where the effect of various degrees of pigmentation is to be determined, and in acceptance, since papers in which titanium dioxide is a component usually sell at a premium price.

3. Purity of Reagents

3.1 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.² 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 ASTM Specification D 1193, for Reagent Water.³

4. Sampling

4.1 Sample the paper in accordance with ASTM Method D 585, Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product.³

5. Sample for Analysis

5.1 Ignite sufficient paper to yield the required amount of ash (Sections 7 and 11) as described in ASTM Method D 586, Test for Ash in Paper.³

¹ These methods are under the jurisdiction of ASTM Committee D-6 on Paper and Paper Products.

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² "Reagent Chemicals, American Chemical Society Specifications," Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopoeia."

³ *Annual Book of ASTM Standards, Part 20.*

METHOD A—QUALITATIVE TEST

6. Reagents

6.1 *Ammonium Sulfate* ((NH₄)₂SO₄).

6.2 *Hydrogen Peroxide* (3%)—Mix 1 volume of concentrated hydrogen peroxide (H₂O₂, 30%) with 10 volumes of water. The solution thus prepared will be sufficiently stable for 5 days.

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

7. Procedure

7.1 Make a qualitative analysis of the ash unless the nature of the loading material is known, since it will facilitate the quantitative analysis.

7.2 For a complete qualitative analysis, proceed in accordance with ASTM Method D 686, Qualitative Examination of Mineral Filler and Mineral Coating of Paper.³

7.3 To test for titanium, place about 0.5 g of ash in a 250-ml beaker, add 20 ml of H₂SO₄ (sp gr 1.84) and 10 g of (NH₄)₂SO₄, and boil for at least 5 min. An insoluble residue indicates silica or siliceous matter. Cool the solution, dilute to 100 ml with water, and heat to boiling. Let settle, and filter through double close-texture, ashless filter paper.⁴ To the filtrate add about 5 to 10 ml of H₂O₂ (3%). A clear yellow to orange-brown color indicates the presence of titanium.

METHOD B—QUANTITATIVE DETERMINATION BY THE VOLUMETRIC METHOD

8. Summary of Method

8.1 The titanium in a dilute sulfuric acid solution is reduced and then titrated with a ferric salt.

9. Apparatus

9.1 *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), a vertical drop of about 6 in. at one end, and a drop of about 4 in. (102 mm) on the other end.

9.2 *Erlenmeyer Flask*, with a wide mouth and 500-ml capacity.

10. Reagents

10.1 *Aluminum Foil*, electrolytic grade.

10.2 *Ammonium Sulfate* ((NH₄)₂SO₄).

10.3 *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 with water. Keep in a well-stoppered, dark-colored bottle.

10.4 *Ferric Ammonium Sulfate Standard Solution* (1 ml = 5 mg TiO₂)—Dissolve 30.16 g of fresh ferric ammonium sulfate (FeNH₄(SO₄)₂ · 12 H₂O) in 800 ml of water containing 15 ml of H₂SO₄ (sp gr 1.84). Add 0.1 N KMnO₄ solution until a very slight pink color is obtained. Dilute to exactly 1 litre and mix well. Filter if cloudy. Standardize, using a 0.1900- to 0.2100-g portion of the National Bureau of Standards standard sample No. 154 of titanium dioxide (TiO₂) and proceed as directed in Section 11. Calculate the TiO₂ equivalent as follows:

$$X = [AB/(C \times 100)]$$

where:

X = TiO₂ equivalent,

A = grams of standard sample of TiO₂ used,

B = percentage of TiO₂ in the standard sample, and

C = millilitres of FeNH₄(SO₄)₂ solution required for titration of the TiO₂.

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

10.6 *Potassium Permanganate Solution* (0.1 N)—Dissolve 3.16 g of potassium permanganate (KMnO₄) in water and dilute to 1 litre.

10.7 *Sodium Bicarbonate, Saturated Solution*—Add 100 g of sodium bicarbonate (NaHCO₃) to 1 litre of water and saturate the solution.

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

11. Procedure

11.1 Weigh to the nearest 0.001 g into the 500-ml Erlenmeyer flask, a sample of ash containing not more than 0.25 g of TiO₂. (Usually 0.25 g of ash is sufficient.)

NOTE 2—If the sample contains more than 1% TiO₂, it is possible to ash 1 g of paper in a platinum crucible. Then the ash is transferred quantitatively to the 500-ml Erlenmeyer flask.

11.2 Add 7 to 9 g of (NH₄)₂SO₄ and 20 ml of H₂SO₄. Mix well and heat on a hot plate until dense white fumes are evolved; then