**Designation: D3720 – 90 (Reapproved 2011)**

# Standard Test Method for
# Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-Ray Diffraction[1]

This standard is issued under the fixed designation D3720; 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 determination of the ratio of anatase to rutile in titanium dioxide pigments. The method is also applicable to pigment mixtures and pigmented coatings containing titanium dioxide.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D215 Practice for the Chemical Analysis of White Linseed Oil Paints (Withdrawn 2005)[3]

D2371 Test Method for Pigment Content of Solvent-Reducible Paints

D2698 Test Method for Determination of the Pigment Content of Solvent-Reducible Paints by High-Speed Centrifuging

D3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings

## 3. Summary of Test Method

3.1 The X-ray diffraction pattern obtained from a material is characteristic of that material. The intensity of a diffraction peak entirely due to one component of a mixture is dependent upon the amount of that substance in the mixture. To a minor extent the peak intensity of the component is also dependent on the mass absorption coefficient of other materials present. Since the test method utilizes the ratio of the intensities of diffraction peaks of two chemically similar materials, it is expected that the effects of other constituents will be the same for both materials.

3.2 The intensity of the diffraction maxima for anatase and rutile is measured by X-ray diffractometry. The intensity of the anatase peak is converted to anatase content relative to rutile and the rutile content is determined by difference.

3.3 The X-ray diffraction measurement is made on single pigments, pigment mixtures, films of pigmented coatings, and films prepared from liquid coatings, if interfering materials are not present. When interfering materials are present, the pigment is separated from the redissolved (or ignited film, or from the liquid coating and treated to isolate the titanium dioxide.

## 4. Significance and Use

4.1 This test method is used by titanium dioxide pigment manufacturers and users for process control and product acceptance.

## 5. Interferences

5.1 Calcium sulfate interferes, but its effect is eliminated by chemical removal (see Practice D215). It is desirable to assure by analysis that any residual $CaSO_4$ is considerably less than the level of anatase being sought. The insoluble residue after removal of calcium sulfate should be ignited above 700°C. Chrome yellow and the valentinite form of antimony trioxide also interfere if not removed. High amounts of iron render analysis difficult due to increased background (see Note 1). Additives, such as antimony and zinc, and impurities, such as niobium and zirconium, are generally present in solid solution and thus would not have interfering diffraction peaks. Surface treatments such as silica and alumina do not interfere. Extreme differences in particle size between the anatase and rutile portions affect the results.

NOTE 1—Background scatter due to high iron levels in a sample may be reduced by use of a cobalt or molybdenum target tube in place of the copper target tube. The background may be eliminated for all practical

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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 D01.31 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] The last approved version of this historical standard is referenced on www.astm.org.

purposes by use of a curved crystal monochromator equipped with a graphite crystal in conjunction with a copper target tube.

5.2 In the calculation of converting the ratio to percent it is implicitly assumed that the sum of anatase and rutile is 100 %, an assumption normally made in $TiO_2$ pigment systems. Other materials present would interfere to the extent that they dilute the sample. The third polymorphic form of $TiO_2$, brookite, would have such an effect. However, it reportedly does not occur in commercial titanium dioxide pigments.

## 6. Apparatus

6.1 *X-Ray Diffractometer*—The principle components of this instrument are: (*a*) X-ray generator, (*b*) copper target X-ray tube, (*c*) goniometer, (*d*) detector, (*e*) electronic circuit panel, (*f*) computer (if used), and (*g*) strip chart recorder or printer.

6.2 *Operating Conditions*—The X-ray tube voltage and filament current and other settings are selected to record X-ray diffraction peaks of weak intensities.

6.2.1 *Nickel Filter,* to remove Cu K beta radiation if a monochromator is not used. Cu K beta radiation will produce a diffraction line from the rutile phase of $TiO_2$ that appears at the same $2\theta$ angle as the anatase analytical line.

6.3 *Typical Apparatus Conditions:*

6.3.1 *High-Voltage Power Supply*—Select X-ray tube voltage, filament current, and other settings so that 0.1 % anatase generates a signal with intensity at least four times the noise level.

6.3.2 *Detector*—Scintillation detector operating at optimum voltage.

6.3.3 *Pulse Height Analyzer*—Settings will depend on instrumentation used.

6.3.4 *Slits*—Receiving slit, 0.15°; others, 1°.

6.3.5 *Chart Speed,* 12.5 mm (½ in.)/min.

6.3.6 *Goniometer Speed,* ¼ °/min, scanning or 0.02° steps with 4.8 s per step.

6.3.7 *Time Constant,* 5.

6.3.8 *Scanning Range,* $2\theta = 28$ to 24°.

6.3.9 *Scale Factors*—For samples of low anatase content a scale factor of 100 counts full scale is normally used for the $2\theta = 26$ to 24° range (anatase diffraction maximum), and a scale factor of 5000 counts full scale is normally used for the $2\theta = 28$ to 26° range (rutile diffraction maximum). The scale factors may be changed depending on the level of anatase expected in the sample.

## 7. Reagents

7.1 *Purity of Reagents*—Untreated rutile and anatase grades of titanium dioxide pigments are used to make synthetic standards for calibration. The crystalline structures of the reagents must be 100 % rutile and 100 % anatase as determined by examining these materials by X-ray diffraction to assure this purity.

7.2 *Mixing Reagents*—A series of rutile standards of varying rutile content are prepared to cover the range of interest by thoroughly mixing known amounts of 100 % rutile and 100 % anatase together. The pigments are dispersed in a solvent such as isopropyl alcohol and then mixed, followed by air drying. This dry cake is ground up using a mortar and pestle to ensure homogeneity.

## 8. Hazards

8.1 X-ray producing equipment can be dangerous to both the operator and persons in the immediate vicinity unless safety precautions are strictly observed. Refer to the manufacturer's instruction manual. Exposure to excessive quantities of X-radiation may be injurious to health. Therefore, users should avoid exposing any parts of their bodies, not only to the direct beam, but also to secondary or scattered radiation that occurs when an X-ray beam strikes or has passed through any material. It is strongly recommended that users check the degree of exposure by film carried on them or by the use of dosimeters and that blood counts be made periodically. Before utilizing the equipment, all persons designated or authorized to operate X-ray instrumentation or supervise its operation, should have a full understanding of its nature and should also become familiar with established safe exposure factors by a careful study of the National Bureau of Standards Handbook "X-Ray Recommendations of the International Roentgen Ray Committee on X-Ray Protection" and other standard publications on the subject. Inquiries should be made of state agencies as to existing requirements.

## 9. Specimen Preparation

9.1 *Powder Samples:*

9.1.1 Packing the specimen in the specimen holder to obtain a planar surface is one of the most important phases in X-ray analysis. Ripples or indentures in the specimen surface cause variations in the test because of an error of eccentricity and a change in the intensities of the peaks. The chance of preferred orientation of pigmentary $TiO_2$ is remote because of its small particle size.

9.1.2 Pack the specimen in a die suitably constructed to accommodate the specimen holder for the goniometer. Apply constant pressure with a hydraulic press (see Note 2). Alternatively, place the specimen holder on a flat, smooth firm surface and pack the specimen into the opening by applying constant and firm pressure with a flat blade. The possibility of variations among different bags of the same lot should be considered.

NOTE 2—Use of a set procedure with a hydraulic press will improve specimen preparation uniformity compared to hand-packed specimens. This is particularly true where more than one person is involved in specimen preparation.

9.2 *Coatings on Metal Panels:*

9.2.1 Cut the coated panel into the proper shape and size to fit an adjustable specimen holder and analyze without further preparation. This assumes that interferences are not present (see Section 5).

9.3 *Liquid Coating Samples:*

9.3.1 Sample material in accordance with Practice D3925.

9.3.2 Liquid coating samples without interfering materials present (see Section 5) are analyzed as cast films of the total paint on aluminum or other suitable substrate. A 25 to 50-µm (1 to 2-mil) dry film thickness is adequate.

9.3.3 Liquid paint samples with interfering materials present (see Section 4) must not be analyzed until the interfering components are removed. This can be accomplished by centrifuging (Test Methods D2371 or D2698) to separate the total pigment. The separated pigment is treated according to the Insoluble Matter section of Practice D215 to obtain interference-free $TiO_2$. Quantitative results are not required for either separation procedure.

## 10. Procedure

10.1 Record the X-ray diffraction maxima of the anatase and of the rutile peak by scanning the range between $2\theta = 26$ to 24° and $2\theta = 28$ to 26°, respectively. Scan each range twice.

10.2 Draw the baseline between the lowest points of the trace on each side of the peak. Measure the peak height above the baseline expressed in chart units, centimetres, counts per second, or other convenient units for the anatase and rutile peaks. Average the net peak heights of the duplicate runs.

10.3 Since only ratios are used, the peak heights need only be corrected for differences, if any, in the scale factors used for the two peaks. Any consistent units can be used, not just counts per second.

10.4 Prior to and after analyzing the unknown sample, analyze one of the standards to verify instrument stability.

## 11. Calculations

11.1 Determine the value of the constant, $K$, as follows

$$K = (I_a/I_r)/(W_a/W_r)$$

where:

$I_a$ = net intensity of the anatase diffraction peak,
$I_r$ = net intensity of the rutile diffraction peak,
$W_a$ = weight of anatase, and
$W_r$ = weight of rutile.

11.1.1 $K$ is equal to the slope of a calibration plot obtained when the intensity ratio $I_a/I_r$ is plotted as a function of $W_a/W_r$, using data derived from a series of standards that span the concentration range of interest. Routine calibration procedures are followed.[4,5]

NOTE 3—The value of $K$ is influenced by the instrument conditions selected in Section 5. Data for standards and test samples must be collected using the same conditions.

11.2 Calculate the anatase level relative to rutile from the peak intensities above background as follows:

$$\text{Percent anatase} = \frac{1}{1 + K\dfrac{I_r}{I_a}} \times 100$$

## 12. Precision

12.1 On the basis of an interlaboratory test of this test method in which four operators in four laboratories tested two materials with composition approaching 100 or 0 % anatase or rutile, the within-laboratory standard deviation was found to be 0.06 % for a single determination. The between-laboratories standard deviation was found to be 0.07 % absolute for results each the mean of two determinations. Based on these standard deviations, the following criteria should be used for judging the precision of results at the 95 % confidence level.

12.1.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.18 % absolute for materials approaching 100 or 0 %.

12.1.2 *Reproducibility*—Two results, each the mean of two determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 0.22 % absolute for materials approaching 100 or 0 %.

## 13. Keywords

13.1 anatase pigment analysis; rutile; titanium oxide analysis; X-ray diffraction

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[4] Myers, H. and Spurr, R., *Analytical Chemistry*, Vol 29, 1957, p. 760.

[5] Zingaro, P. W., *Norelco Reporter*, Vol 5, No. 5–6.