



Standard Test Method for Determination by X-ray Fluorescence Spectroscopy of Titanium Dioxide Content in Paint¹

This standard is issued under the fixed designation D 4764; 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.

^{ε1} NOTE—Keywords were added editorially in April 1993.

1. Scope

1.1 This test method covers the determination of titanium dioxide content in liquid paint. This test method is applicable to both water-reducible and solvent-reducible paints.

1.2 *This standard does not purport to address all of the safety problems, 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 hazards statements are given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 476 Specification for Titanium Dioxide Pigments²

D 1193 Specifications for Reagent Water³

D 1394 Test Methods for Chemical Analysis of White Titanium Pigments²

D 2369 Test Method for Volatile Content of Coatings⁴

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings⁴

D 3980 Practice for Interlaboratory Testing of Paint and Related Materials⁴

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals⁵

3. Summary of Test Method

3.1 Paint containing a known amount of titanium dioxide is used as the reference standard. A solution of tetraethylammonium bromide in 2-ethoxyethanol is added to the standard paint and to each paint being analyzed. Drawdown films of the standard and test paint are made on thin plastic sheets. The intensities of key X-ray fluorescence peaks of titanium and bromine are measured. The titanium dioxide content is deter-

mined by comparing the ratio of the intensities of titanium and bromine peaks in the test paint and the standard. Differences in the nonvolatile content of the paints are taken into account in the calculation of results.

4. Significance and Use

4.1 Titanium dioxide pigments are components with high refractive index that significantly influence the opacity, color, durability, and other properties of coatings. This test method for determining titanium dioxide content is quicker and easier to use than Test Methods D 1394, a wet chemical analysis method for pigments. It is conveniently applicable to single samples and to large numbers of samples. Only a single relatively stable reagent used to prepare standards and paints under test need be stored. Drawdown specimens used as standards, once prepared, can be stored indefinitely and used repeatedly.

5. Apparatus

5.1 *X-ray Fluorescence Spectrometer*, suitable for measurement of the baseline corrected intensity of the K α lines of titanium and of bromine. For spectrometers equipped with a tungsten or chromium target and a lithium fluoride (200) analyzing crystal, these lines are observed at 2 θ angles of 86.09° and 29.97°, respectively.

NOTE 1—Follow the recommendations of the manufacturer of the instrument used. Use operating conditions that ensure that the count rate for bromine and titanium are within the linear response range of the detector. Although the base operating conditions and count rate may be different for different instruments, these differences will not affect the outcome of the analysis.

5.2 Paint Shaker.

5.3 *Film Applicator*, to produce a 3-mil (75- μ m) wet film thickness.

5.4 *Plastic Sheet*,⁶ with no interfering X-ray fluorescence peaks and not attacked by paint solvent.

5.5 *Perforated Suction Plate*, or other flat surface.

5.6 *Vials and caps*, 20 mL.

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.

Current edition approved Feb. 26, 1988. Published April 1988.

² *Annual Book of ASTM Standards*, Vol 06.03.

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 06.01.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ Leneta P-121-10N dull black plastic panels 6½ by 17 in. by 10 mils (165 by 432 by 0.25 mm) in size, available from Leneta Co., 15 Whitney Rd., Mahwah, NJ 07430, have been found suitable for this purpose.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests, unless otherwise specified. It is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁷ 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that conforms to the requirements of Type II of Specification D 1193.

6.3 *2-ethoxyethanol*, purified grade.

6.4 *Tetraethylammonium Bromide*, internal standard solution—Into a 100-mL volumetric flask weigh approximately 10.80 g of tetraethylammonium bromide (TEAB) to 1 mg. Dissolve the TEAB in 2-ethoxyethanol, fill the flask to the mark with 2-ethoxyethanol, and mix thoroughly. (TEAB dissolved in 2-ethoxyethanol can be used as an internal standard for both water-reducible and solvent-reducible paint. However, water may be substituted for 2-ethoxyethanol, if only water-reducible paint is to be analyzed.)

7. Hazards

7.1 As exposure to excessive quantities of x-radiation is injurious to health, X-ray producing equipment can be dangerous to both the operator and persons in the immediate vicinity unless safety precautions are strictly observed. 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 passes 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,"⁸ the manufacturer's instruction manual, and other standard publications on the subject. Inquiries should be made of state agencies as to existing requirements.

8. Specimen Preparation

8.1 Thoroughly mix and sample each paint in accordance with Practice D 3925. Prepare duplicate specimens of the standard paint, which contains a known concentration of

titanium dioxide, and each test paint using the following procedure. Into a 20-mL vial weigh approximately 7.00 g of paint to 1 mg. Pipet 2 mL of TEAB internal standard solution (see 6.4) into the paint and thoroughly mix.

TABLE 1 Instrument Conditions

	Ti K α	Br K α
Analyzer crystal	LiF	LiF
Counter	Flow or Scintillation	Scintillation
Collimator	Fine	Coarse
Order	First	First
Tube KV/mA	10/5	60/24
Time, s	20	20
Peak, 2 θ ,°	86.09	29.97
Background, 2 θ ,°	85.00	29.00

8.2 Place a plastic sheet on the perforated suction plate. On the plastic sheet make a 3.0-mil (75- μ m) thick drawdown of the liquid paint. Air dry the drawdown film overnight. Cut from the drawdown on the plastic sheet a disk of a size appropriate for the specimen holder of the spectrometer.

8.3 Determine the percent nonvolatile content of each paint at 110°C in accordance with Test Method D 2369 if the information is not already available.

9. Procedure

9.1 Turn on the spectrometer and allow it to stabilize thoroughly before beginning collection of results. With the aid of the manufacturer's literature, select spectrometer settings to permit measurement of the intensity of the K α peaks of titanium and bromine. For instruments equipped with an X-ray tube with a tungsten or chromium target, the settings prescribed in Table 1 may be used as guidelines (Note 1).

9.2 Place the disk in the specimen holder in such a way that the coated side of the sheet is turned toward the incident X-rays. Before measuring the specimens, record the background spectrum in the ranges of the K α peaks of titanium and bromine, including at least 10° on each side. Check the spectra for the presence of interfering peaks and select for each peak an angle for background measurement where interference is at a minimum.

9.3 At the selected angles measure the background intensities and the intensities of the K α peaks of titanium and bromine in counts per second (c/s). Determine the net intensity, c/s, of each peak by subtracting the background count from the peak count.

10. Calculation

10.1 Use the values of the standard paint of known TiO₂ content to calculate K_t , the reference intensity ratio of titanium relative to bromine in the film, defined as:^{9,10}

$$K_t = \frac{\frac{B}{B+N} \times \frac{I_t}{I_b}}{\frac{T}{T}} = \frac{B}{T} \times \frac{I_t}{I_b} \quad (1)$$

⁷ *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁸ Available from National Bureau of Standards, National Center for Standards, Gaithersburg, MD 20899.

⁹ Chung, F. H., "A New Approach to Quantitative Multi-element X-ray Fluorescence Analysis," *Advances in X-ray Analysis*, 19, 1976, p. 81.

¹⁰ Chung, F. H., Lentz, A. J., and Scott, R. W., "A Versatile Thin Film Method for Quantitative X-ray Emission Analysis," *X-ray Spectrometry*, 3(4), 1974, p. 172.

where:

- B = TEAB used in making film, g,
 = TEAB used, g, $\times \frac{2 \text{ mL}}{100 \text{ mL}}$ = TEAB used, g, $\times \frac{1}{50}$
 T = TiO_2 in film, g,
 = paint used, g, $\times (\% \text{ TiO}_2 \text{ in dry paint}/100) \times \% \text{ non-volatile matter}/100$,
 = paint used, g, $\times \% \text{ TiO}_2 \text{ in liquid paint}/100$,
 = paint used, g, $\times \text{weight fraction of TiO}_2 \text{ in liquid paint}$,
 N = nonvolatile matter (from paint) in film, g,
 = paint used, g, $\times \% \text{ nonvolatile matter}/100$,
 = paint used, g, $\times \% \text{ weight fraction of nonvolatile matter}$,
 I_b = intensity of bromine peak, c/s, and
 I_t = intensity of titanium peak, c/s.

Therefore

$$K_t = \frac{B}{W} \times \frac{1}{50X} \times \frac{I_t}{I_b} \quad (2)$$

where:

- W = paint used, g, and
 X = weight fraction of TiO_2 in liquid paint.

Calculate the mean of the K_t values obtained from the two disks coated with the standard paint and use in the calculation in 10.2.

10.2 Calculate the percent TiO_2 in the test paint, P , as follows:

$$P = \frac{2 \times B \times I_t}{K_t \times W \times I_b} \quad (3)$$

where the symbols are defined as in 10.1.

10.3 Sample Calculation:

10.3.1 Reference intensity ratio, K_t ,

Standard paint—12.8 % TiO_2 in liquid paint,

Standard solution—10.347 g TEAB in 100-mL solution,

Film—2 mL of standard solution in 7.25 g of liquid standard paint, and

X-ray intensity: $I_b = 4396 \text{ c/s}$, $I_t = 1804 \text{ c/s}$.

$$K_t = \frac{10.347}{7.252} \times \frac{1}{(50)(0.128)} \times \frac{1804}{4396} = 0.0915 \quad (4)$$

The mean of duplicate analyses is $K_t = 0.0916$.

10.3.2 TiO_2 content of test paint,

Data:

Film—2 mL of standard solution in 7.186 g wet paint, and

X-ray intensity: $I_b = 4272 \text{ c/s}$, $I_t = 2569 \text{ c/s}$

$$P = \frac{10.347}{7.186} \times \frac{2}{0.0916} \times \frac{2569}{4272} = 18.9 \% \quad (5)$$

11. Precision and Bias

11.1 In an interlaboratory study of this test method, one operator in each of five laboratories analyzed on two days two samples of latex house paint and two samples of solvent-reducible house paint. The mean weight percent titanium dioxide in samples Number 1 through 4 was, respectively, 3.64, 19.1, 7.44, and 15.8 %. The pooled within-laboratory coefficient of variation was 2.39 % with 19 df and the pooled between-laboratories coefficient of variation 4.47 % with 15 df, after discarding one duplicate value from one laboratory because the range differed significantly from all other duplicate ranges for paint sample Number 2. Based on these coefficients of variation, the following criteria should be used for judging the acceptability of results at the 95 % confidence level (see practices D 3980 and E 180):

11.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 7.08 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 13.5 % relative.

12. Keywords

12.1 titanium dioxide content; XRF spectroscopy

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.