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Ti-Pure®

TITANIUM DIOXIDE

CONCENTRATED ACID SOLUBILITY OF TiO₂

METHOD: T4400.315.07.WP

TITANIUM DIOXIDE
(Ti-Pure®)

Determination of Acid Solubility of TiO₂ by Spectrophotometer
(TP-109.2)

I. Principle

TiO₂ is a basic oxide and will react with concentrated sulfuric acid to produce a soluble species. After adding hydrogen peroxide, the soluble TiO₂ can be measured on a spectrophotometer, reading absorbance at 400 mμ. A continuous coating of SiO₂, on the TiO₂, will prevent the dissolution of TiO₂. The test measures the effectiveness of the SiO₂ coating.

II. Applicability

This method applies directly to the determination of acid solubility of TiO₂ coated with insoluble inorganic oxides to determine the effectiveness of the inorganic coating.

III. Limitations

It has been demonstrated that improved precision is obtainable by imposing tight controls on the test variables of time and temperature of acid digestion, keeping the apparatus in a draft-free environment, keeping Tuttle covers in place and carefully adding the pigment so that none gets hung up on the wall of the test tube. In addition, absolute cleanliness of all equipment is necessary. Traces of soap or any organic will discolor the sulfuric acid and interfere with the subsequent spectrophotometric analysis.

IV. Sensitivity, Precision and Accuracy

A. Sensitivity

No data are available.

B. Precision

1. Single Operator

The average analyses (\bar{X}), standard deviation (s), and 95% confidence limit (95% CL) established for the single operator precision of the method were as follows:

	\bar{X}	s	95%CL
% Acid Solubility	7.040	0.435	± 0.826

The above data were calculated from 8 replicate analyses of 1 sample of R-960 performed by 1 technician over several days.

2. Multiple Operator

The average analysis (\bar{X}), standard deviation (s), and 95% confidence limits (95% CL) established for the multiple operator precision of the method were as follows:

	\bar{X}	s	95%CL
% Acid Solubility	7.370	0.471	± 0.895

The above data were calculated from 32 replicate analyses of 1 sample of R-960 performed by 8 technicians, 2 tests on each of 2 days.

C. Accuracy

No data are available but results have been satisfactory based on experience.

V. Special Apparatus (Equivalent apparatus may be substituted)

1. Magnetic stirrer with hot plate 9" x 9", Model #4817, Cole-Parmer Instrument Co., Chicago, IL.

2. Immersion probe for use with above, Model #4812-1, Cole-Parmer Instrument Co., Chicago, IL.
3. Thermometer, 1°C - 201°C., #15-043, Fischer Scientific.
Thermometer is calibrated vs. a certified thermometer.
4. Aluminum heating block fabricated locally to contain 13 test tubes (100 x 25 mm), thermometer and immersion probe. The top and sides are covered with Kaowool Ceramic cement, a substitute for asbestos cloth, Babcock & Wilcox, Birmingham AL., or equivalent insulation.
5. Test tubes 100 x 25 mm, #9800-25, Corning Glass Co., Corning, NY, if available. If not available, obtain 150 x 25 mm (same supplier) and have them cut down to 100 mm locally.

Quartz tubes have proven equal to the above and are preferred because of improved durability. Ace Glass Company, Part #30738-000.
6. Tuttle covers, #10-042A, Fisher Scientific.
7. Magnetic Stirring bars, Teflon® coated, 1/2" x 5/16", #4770-2, Cole-Parmer Instrument Co., Chicago IL.
8. Volumetric flasks, ASTM certified, class A, 25 mL #10-211A, 100 mL 10-211C, Fisher Scientific.
9. Disposable containers with lids (4-oz cap), Containers #11-838-15, Lids #11-834-2Y, Fisher Scientific.
10. Ice Crusher by Oster #571-06, Oster Division of Sunbeam Corp., Milwaukee, WI.
11. Micrometer Dispenser, 10 mL, with flask #7892, Cole-Parmer Instrument Co., Chicago, IL.
12. Test tube rack, #14-7800, Fisher Scientific Co.
13. Syringe, Plastipak, disposable, 10 mL, #14-823-50, Fisher Scientific Co.
14. Funnel, polypropylene, #10-320-8D, Fisher Scientific Co.
15. Filter paper, Whatman #5, 18.5 cm.
16. Spectrophotometer, Bausch & Lomb, Model 21.

17. Spectrophotometric cell, 10 mm light path. Calibrated vs. Certified set, traceable to NIST.
18. Weighing paper, S&S #B-2, 3 x 3 in, #9-898-10A, Fisher Scientific Co. (or aluminum dishes).

VI. Reagents (Reagent grade except as noted)

1. Sulfuric acid, 66° Be (concentrated), ACS certified.
2. Sulfuric acid, 10% v/v, ACS certified, Tennessee Reagents.
3. Hydrogen Peroxide, 30%, ACS certified.
4. Crushed Ice made from distilled water.
5. Ammonium Sulfate, 99.5% purity, ACS certified, available from local Fisher Scientific.

VII. Special Safety Considerations

A. Product Hazards

There are no unusual product hazards. However, titanium dioxide is regulated as an air contaminant and care should be exercised to minimize product dusting. Wipe up all spills with a damp paper towel. Refer to MSDS #2816CR for more information on Titanium Dioxide.

B. Procedure Hazards

1. Hot Plate - "High Heat"- use tongs when handling hot glassware. Always use hot plate under hood to avoid acid fumes.
2. Glassware - inspect for chips and cracks before using. Careful examination of the bottoms of the test tubes is very important. Discard if scratched or chipped.
3. Ice Crusher - Keep fingers clear of blades.
4. Sulfuric Acid - Can cause severe burns, especially when hot. Extreme care must be used at all times. A full face shield and Neoprene gloves must be worn.

NOTE: Sulfuric Acid is extremely irritating in vapor or liquid form, especially when hot. Use only in a well-ventilated area. Neoprene gloves and face shield must be worn when handling. "ALWAYS POUR ACID INTO WATER—NOT WATER INTO ACID EXCEPT IN CERTAIN CAREFULLY CONTROLLED CASES WHEN IT IS NECESSARY TO THE TEST, AND THEN FOLLOW THE PROCEDURE WITH EXTREME CARE."

5. 30% Hydrogen Peroxide - Very strong oxidizing agent. Do not mix with organic materials or peroxidizables. Use full face shield and rubber gloves when handling.
6. Refer to Material Safety Data Sheets for any chemical used in this test with which you are not familiar.

VIII. Procedure

A. Operating Conditions

Refer to the manufacturer's operating instructions for the spectrophotometer.

B. Calibration

Preparation of Spectrophotometric Curve

1. Weigh exactly 1.0118 g of the (DUPONT 98.83% TiO₂ ANALYTICAL STANDARD Ti-Pure®) and transfer to a 300-mL Erlenmeyer flask.
2. Add 15 ± 0.1 g ammonium sulfate and 20 ± 0.1 mL of concentrated sulfuric acid.
3. Place Tuttle cover in mouth of the flask, mix thoroughly by swirling, then heat gently to complete solution.
4. Cool to room temperature, then CAREFULLY DILUTE SOLUTION WITH APPROXIMATELY 80 mL OF DISTILLED WATER and transfer to 1-L, CLASS A, volumetric flask. (This step is in violation of the generally accepted rule of not adding water to acid but is necessary to the test and with care can be done safely.) Rinse flask with distilled water, adding washings to volumetric flask. Dilute further with distilled water to about 800 mL. Carefully add 80 mL of concentrated sulfuric acid, mix and cool to room temperature. Dilute to 1000 mL mark with distilled water.

5. This solution contains 0.001 g TiO₂/mL. Let stand one week before using.
6. Transfer 2 ± 0.01 mL of the standard TiO₂ solution, using a class A pipette, to a 100-mL, class A, volumetric flask.
7. Add 10 ± 0.1 mL of 30% hydrogen peroxide with a disposable 10 mL plastic syringe.
8. Dilute to volume, using 10% sulfuric acid and mix.
9. Repeat Steps 6, 7 and 8 using 4, 6 and 8 mL of standard solution.
10. To prepare a reference solution, add 10 ± 0.1 mL of 30% hydrogen peroxide to a 100 mL, Class A, volumetric flask with a 10 mL plastic syringe, and dilute to 100 mL mark with with 10% sulfuric acid.
11. Allow to stand at least 1 hour before reading absorbance.
12. Values of the four samples prepared above are 20, 40, 60 and 80 mg TiO₂/L.
13. To convert mg/L TiO₂ to % soluble TiO₂, divide mg/L TiO₂ by 8.

* See Appendix 3 for information on where the factor 8 comes from.
14. Read absorbance of the 4 standard solutions against the reference solution at 400 mμ using 10-mm cell. Record results to two decimal places.
15. Construct a spectrophotometric curve on graph paper of absorbance vs. % soluble TiO₂. Example of such a curve is shown in Appendix 1.

C. Sampling

1. Samples are normally supplied by manufacturing.

D. Sample Analysis

1. On the day of testing, working in the hood, place aluminum heating block on magnetic stirrer/hot plate. (A shield should be placed around the hot plate and heating block to prevent drafts from affecting the temperature of the block during the

test). Insert remote temperature sensor and thermometer into the appropriate thermal wells in the heating block. Adjust temperature to $175 \pm 2^\circ\text{C}$. The top and sides of the aluminum block are covered with Kaowool Ceramic Cement (or equivalent insulation) to limit the heat loss.

2. Fill the required number of disposable 4-oz containers approximately 1/4 full with crushed ice made from distilled water. Fasten lids and store in the freezer, until ready for use.
3. Absolute cleanliness of all equipment is necessary. Traces of soap or any organic material will discolor the sulfuric acid and interfere with the subsequent colorimetric analysis.
4. Place a magnetic stirring bar into each test tube.
5. Add 10 ± 0.01 mL 66° (concentrated) sulfuric acid to the test tubes using micrometer dispenser.
6. Place each test tube in the appropriate position in the heating block and cap each tube with a Tuttle cover. Adjust magnetic stirrer to position 7. Before inserting test tube into block make sure the outside of the tube is dry. Moisture on the outside of the tube, inserted into the hot block, could form steam, causing the tube and contents to blow out of the block and cause an injury.
7. Weigh 0.2000 ± 0.0005 g of each sample and standard on weighing papers or aluminum dishes, and set aside.
8. After approximately 15 - 30 minutes the temperature of the block should have again reached $175 \pm 2^\circ\text{C}$. Add the samples and standard to the sulfuric acid at 15 second intervals, noting the time when the first sample was added. Add pigment so that a minimum amount adheres to the side of the tube. Replace Tuttle covers.
9. Digest samples for 60 ± 1 minute.
10. About three minutes before the end of the digestion period, arrange numbered plastic containers of crushed ice near the work area in the hood. If timing is correct, there will be no ice melted before sample is added.

11. After one hour digestion, remove Tuttle cover, grasp test tube with tongs and quench by rapidly pouring contents into container of crushed ice. After digestion mixture is poured, put test tube into container, mouth down. Full face shield and apron must be worn. The use of a safety shield is recommended. The tubes must be quenched at 15 second intervals (as in loading) to give all tubes the same one hour digestion period.
12. Wash residue in test tubes using distilled water and collect washings in container from which test tube was removed.
13. Transfer contents of plastic container into a 100-mL, Class A, volumetric flask. Wash container with distilled water, collecting washings in the volumetric flask.
14. Dilute to the 100 mL mark on the flask with distilled water, stopper and mix thoroughly.
15. Filter sample by gravity using two, #5, 18.5 cm Whatman filter papers. Collect the filtrate in the original 4-oz. container after washing and drying. The filtrate must be clear and free of turbidity. Refilter if the slightest sign of turbidity is present. Yellow to black color indicates sign of organics.
16. Using a disposable 10 mL plastic syringe, add 10 ± 0.1 mL of filtrate to a 25-mL, Class A, volumetric flask.
17. Add 2 ± 0.1 mL 30% hydrogen peroxide using a 10 mL plastic syringe.
18. Dilute to volume with 10% sulfuric acid. Stopper and mix well.
19. Prepare a blank by taking 2 ± 0.1 mL 30% hydrogen peroxide and diluting to 25 mL mark with 10% sulfuric acid in a Class A volumetric flask.
20. Turn on spectrophotometer and allow samples to stand at least 1 hour before reading.
21. Read absorbance of standard and samples using a 10 mm cell. Set spectrophotometer at 400 m μ . Cell must be thoroughly cleaned and checked before using. Record the result to two decimal places.

22. If the final color is so intense that it cannot be read on the spectrophotometer, use a smaller aliquot (5 mL, 2 mL or 1 mL); starting with Step 15 above. See Step 4 in Calculation for compensating calculation.

E. Calculations

The absorbance reading is entered into the CQMS Acid Sol. Program in the computer and the computer calculates and reports the results.

NOTE: If the computer is not available, the following calculation should be used:

1. Convert absorbance reading to % soluble TiO₂ using chart in Appendix 1. (The chart was prepared in Section VIII-B above.)
2. Correct measured values of % soluble TiO₂ by multiplying the measured value by a correction factor. This factor is obtained by dividing the standard value of % solubility by the measured value of % solubility of that standard. Report result to one decimal place.

Calculation of correction factor:

$$\text{Correction Factor} = \frac{\text{Actual value of \% solubility of standard}}{\text{Measured value of \% solubility of standard}}$$

Calculation of corrected value of % solubility of a sample:

$$\text{Corrected value} = \text{Correction factor} \times \text{Measured value}$$

3. Example using 2.98% solubility standard

	Standard	Sample
Actual % sol. TiO ₂	2.98	----
Absorbance Reading	0.20	0.28
mg/L TiO ₂	20.8	28.6
Measured % sol. TiO ₂	2.600	3.575

$$\text{Correction Factor} = 2.98/2.600 = 1.1462$$

$$\text{Corrected \% Soluble TiO}_2 = 1.1462 \times 3.575 = 4.1\%$$

4. If smaller aliquots were used because of intense color development, the final % soluble TiO₂ is multiplied by a factor selected from below according to the volume of sample.

Vol. of Sample	Factor
5 mL	X2
2 mL	X5
1 mL	X10

IX. Quality Control

Use appropriate Statistical Process Control procedures as established in the site Control Lab for this test. (Absorbance of standard is recommended).

X. Comments

Acid solubility has been used as a method of determining the extent that inorganic additives have protected the titanium dioxide from the vehicle.

XI. References

None

XII. Appendix

1. An Example of an Acid Solubility Chart (absorbance vs. % solubility).
2. Aluminum Block.

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APPENDIX 1

PERCENT SOLUBLE TITANIUM DIOXIDE AS A FUNCTION OF OPTICAL DENSITY AT
400 μm
(Typical Curve)

"Contact Methods Manager for hard copy"

APPENDIX 2

DESIGN OF ALUMINUM BLOCK

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