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WI _____ 250100.01 _____

T _____ 627 _____

BALLOT NO. _____ 02-SARG _____

DRAFT NO. _____ 01 _____

DATE _____ October 16, 2025 _____

WORKING GROUP
CHAIR _____ N/A _____

SUBJECT
CATEGORY _____ CPSE _____

RELATED
METHODS _____ See "Additional Information" _____

CAUTION:

This Test Method may include safety precautions which are believed to be appropriate at the time of publication of the method. The intent of these is to alert the user of the method to safety issues related to such use. The user is responsible for determining that the safety precautions are complete and are appropriate to their use of the method, and for ensuring that suitable safety practices have not changed since publication of the method. This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this method, the user must determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Determination of Titanium Dioxide

(Ten-year review of Classical Method T 627 cm-16)

1. Scope

1.1 This method describes a procedure for the volumetric quantitative determination of titanium dioxide (TiO₂) in paper and raw materials such as pigments, fillers, and minerals, as well as in materials in various stages of process such as white water, modified or unmodified coating colors, inks, etc. It is suitable for all levels of TiO₂ content.

1.2 TAPPI T 421 "Qualitative (Including Optical Microscopic) Analysis of Mineral Filler and Mineral Coating of Paper" describes a qualitative procedure for determining the presence or absence of titanium in paper.

2. Summary

The titanium, in a dilute sulfuric acid solution, is reduced with aluminum (*I*) and determined volumetrically by titrating with standardized ferric ammonium sulfate solution.

3. Significance

3.1 The accurate determination of titanium dioxide is essential to economical paper mill operation, especially when it is used as a filler material.

3.2 Results obtained by this method will include chromium, antimony, and any other substance which is reduced by aluminum and subsequently oxidized by ferric ions. However, appreciable quantities of interfering materials are usually not likely to be encountered.

4. Apparatus

4.1 *Reduction apparatus*, shown in Fig. 1. It comprises a stoppered 500 mL Erlenmeyer flask with a 5-mm delivery tube leading to a 250 mL beaker and a glass rod extending downward from the stopper to hold a piece of aluminum foil.

4.2 *Ashing equipment*: a silica, or preferably a platinum, dish and a muffle furnace at $925 \pm 25^\circ\text{C}$.

4.3 *Vycor beaker*, 250 mL.

4.4 *Zirconium crucible*, 30 mL.

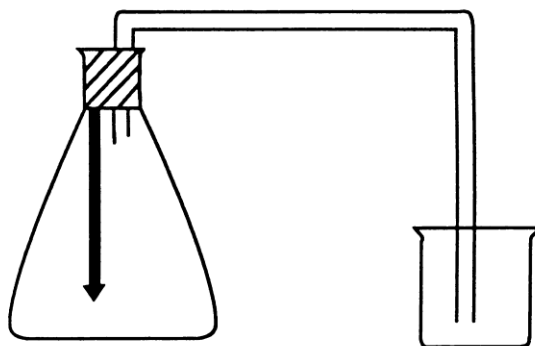


Fig. 1. Apparatus for aluminum reduction.

5. Reagents

5.1 *Dissolving solution*

5.1.1 *Ammonium sulfate*, $(\text{NH}_4)_2\text{SO}_4$.

5.1.2 *Sulfuric acid*, concentrated H_2SO_4 .

5.1.3 Heat together 100 g of ammonium sulfate and 180 mL of concentrated sulfuric acid until the salt is dissolved and light fumes appear. Cool and store in a glass stoppered bottle.

5.2 *Hydrochloric acid*, concentrated HCl.

5.3 *Aluminum metal foil*, electrolytic grade, preferably about 0.2 mm (0.008 in.) thick.

5.4 *Standard titanium dioxide*, obtainable from the National Institute of Standards and Technology (NIST), with analysis.

5.5 *Hydrogen peroxide*, reagent grade.

5.6 *Hydrogen peroxide*, 3% H_2O_2 . Dilute 10 mL of 30% H_2O_2 to 100 mL with distilled water. This solution is sufficiently stable for 5 days.

5.7 *Standardized ferric ammonium sulfate solution*. Dissolve 30.16 g of fresh $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ in 800 mL of distilled water containing 15 mL of concentrated H_2SO_4 . Add 10 mL 3% H_2O_2 and boil until O_2 is no longer evolved; dilute to exactly 1000 mL and mix well. Filter if cloudy. Standardize against the standard TiO_2 solution using 0.1900 to 0.2100 g of TiO_2 and following the same procedure as for paper ash or pigments. Calculate the solution factor as follows:

$$\text{Factor} = \frac{\text{g NIST TiO}_2 \times \% \text{TiO}_2 \text{ in NIST TiO}_2}{\text{mL of titrant} \times 100}$$

This factor should be about 0.005 g of TiO_2 per mL of the solution.

5.8 *Ammonium thiocyanate indicator*. Dissolve 24.5 g of NH_4SCN in 80 mL of hot distilled water, filter, bring to room temperature, and make up to 100 mL in a graduated cylinder with distilled water. Keep in a well-

stoppered, dark-colored bottle.

5.9 *Sodium bicarbonate solution.* Prepare a saturated solution with distilled water at the time of analysis. About 17 g of NaHCO_3 added to 150 mL of water will be required (may be replaced with water if the carbon dioxide cylinder is used).

5.10 *Potassium pyrosulfate*, $\text{K}_2\text{S}_2\text{O}_7$, reagent grade (for fusing mineral specimens).

5.11 *Carbon dioxide* (optional), cylinder of compressed CO_2 .

6. Sampling and test specimens

6.1 The indicated sample quantities will provide three test specimens.

6.2 *Paper*

6.2.1 Obtain a sample in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Products" sufficient to yield 1.5 g of ash.

6.3 *Fillers, pigments, and minerals*

6.3.1 Obtain a 1.5 g sample in accordance with TAPPI T 657 "Sampling of Fillers and Pigments."

6.4 *White water*

6.4.1 Obtain a sample in accordance with TAPPI T 656 "Measuring, Sampling, and Analyzing White Waters" sufficient to yield 1.5 g of ash derived from the total suspended solids as determined in T 656.

7. Procedure

7.1 *For paper*

7.1.1 Determine moisture content in accordance with TAPPI T 412 "Moisture in Paper and Paperboard."

7.1.2 Ash the paper in accordance with TAPPI T 413 "Ash in Paper and Paperboard," obtaining a 0.5 g test unit of ash.

7.1.3 Accurately weight a portion to contain from 0.05 to not over 0.25 g of TiO_2 and put into the 500 mL flask of the reduction apparatus. Usually 0.5 g of ash is sufficient.

NOTE 1: If only the percentage of TiO_2 in the paper, and not the proportional amount of TiO_2 in the ash, is required, ash a weighed portion of the paper in a platinum crucible and transfer quantitatively to the 500 mL flask.

7.1.4 Add 25 mL of dissolving solution (5.1) to the flask. Heat on a hot plate until fumes of SO_3 are evolved. Continue to heat strongly until solution is complete or it is apparent that the residue is composed of siliceous matter.

NOTE 2: If the above procedure does not bring the test specimen into solution and the analysis requires total TiO_2 , including that portion in clay, then try the following Na_2O_2 method: transfer a 0.5000 g test unit into a 30 mL zirconium crucible. Mix with 5 g Na_2O_2 . Fuse sample over a Meker burner while rotating the crucible of the sample. When the crucible has cooled slightly, place it in a 250 mL beaker. Pour 60 mL of distilled water into the beaker and immediately cover the beaker with a watch glass. After the melt has completely dissolved, remove the crucible and lid with tongs and rinse both with distilled water. Carefully pour 60 mL of 9M H_2SO_4 into the beaker. If the solution color is weaker than approximately 0.05N potassium dichromate, the test can be finished according to A.5.4. If the solution color is stronger, add 20 mL 12M HCl and boil for 5 min to decompose peroxides. Remove from the burner and proceed as under 7.5.

7.2 *For ores and minerals.* Accurately weight a test specimen of about 0.5 g into a 250 mL Vycor beaker containing 15 g or more of $\text{K}_2\text{S}_2\text{O}_7$. Cover the beaker with a watch glass and fuse over a Meker burner for approximately $\frac{1}{2}$ h. Cool, add 150 mL of H_2O and 18 mL of concentrated H_2SO_4 and boil to dissolve. When the specimen is dissolved, transfer it to the Erlenmeyer flask of the reduction apparatus, add 20 mL of concentrated HCl and boil again. Remove from the burner. Proceed as under 7.5. This test method calculation would need to be altered for samples suspected of containing chromium and vanadium.

NOTE 3: If the above procedure does not bring the test unit into solution, use the procedure outlined in Note 2.

7.3 *For pigments.* Accurately weigh about 0.2000 g into a 500 mL Erlenmeyer flask, add 25 g of $(\text{NH}_4)_2\text{SO}_4$ and 25 mL of concentrated H_2SO_4 and boil over the flame of a Meker burner. Remove from burner, cool, add 130 mL of distilled water and 20 mL of concentrated HCl. Boil again, remove from the burner, and proceed as under 7.5.

7.4 *For white water*

7.4.1 Determine total suspended solids according to T 656.

7.4.2 Determine fixed suspended solids according to T 656.

7.4.3 Using the ash from 7.4.2, proceed as in 7.1.3.

7.5 *Reduction and titration.* Insert the short end of the delivery tube into one hole of the two-hole stopper for the 500 mL flask. Insert the glass rod having the slight hook or collar at the bottom into the other hole of the stopper as shown. Attach approximately 1 g of aluminum foil to the bottom end of the rod by coiling and crumpling it around the rod. It is usually desirable to fold the aluminum foil one or more times to reduce the rate of reaction.

7.5.1 Push the stopper, with the foil and delivery tube, into the flask, and at the same time submerge the long end of the delivery tube in the 250 mL beaker containing about 200 mL of the NaHCO₃ solution.

7.5.2 As soon as the aluminum has dissolved, gently boil the contents of the flask for 3 to 5 min without removing the delivery tube. Carefully cool to less than 60°C, preferably by partial immersion of the flask into a vessel of water. The NaHCO₃ solution will be sucked into the flask during this cooling, and with a rapid reaction will give an atmosphere of CO₂ over the reduced titanium solution. Withdraw the stopper, but before removing the stopper, rod, and delivery tube completely, rinse the glass rod attached to it with a little distilled water, catching the rinse water in the flask. Add 2 mL of the NH₄SCN indicator and titrate immediately with ferric ammonium sulfate to a straw-colored end point. It is best to add the bulk of the ferric solution rapidly and then, after shaking, finish the titration drop by drop.

NOTE 4: Instead of using the CO₂ generated from the NaHCO₃ solution provide the required protective atmosphere, the CO₂ may be supplied from the cylinder through a connection to an inlet tube added to a three-hole stopper for the 500 mL flask. If a CO₂ cylinder is employed, attach it to an inlet tube provided in the stopper of the flask and flush out the connecting tubing to remove the air and allow a very slow stream of CO₂ to continue to pass during the reduction. After the reduction and when the solution in the flask has been boiled 3 to 5 min, pass CO₂ into the flask before removing the heat to prevent the liquid in the beaker from being sucked back. If the CO₂ cylinder is used, water may be substituted for the NaHCO₃ solution in the beaker.

7.6 Calculate the percentage of TiO₂ in the specimen from the titration and the factor of the solution as follows:

$$\% \text{ TiO}_2 = \frac{\text{mL of titrant} \times \text{factor} \times 100}{\text{weight of specimen, g}}$$

7.6.1 Calculate percent TiO₂ in paper by dividing percent TiO₂ from 7.6 by the percent ash determined in 7.1.2.

7.7 *Report.* The averages of three tests make up a test result.

7.7.1 Report the percentage of TiO₂ in paper on the moisture free weight to the nearest 0.1%.

7.7.2 Report the percentage of TiO₂ in other materials as an “as received” or on total solids basis as desired and so indicate with the report.

8. Precision

8.1 *In paper ash*

8.1.1 Repeatability (within a laboratory) = at 5% level, 3.58%; at 40% level, 0.94%; at 60% level, 1.61%.

8.1.2 Reproducibility (between laboratories) = at 5% level, 11.66%; at 40% level, 1.01%; at 60% level, 1.75%.

8.1.3 Comparability (between materials) = not known; in accordance with the definition of these terms in TAPPI T 1200 “Interlaboratory Evaluation of Test Methods to Determine TAPPI Repeatability and Reproducibility.”

9. Keywords

Titanium dioxide, Paper, Pigments, Fillers, Minerals, White water, Coating color, Ink

10. Additional information

10.1 Effective date of issue: To Be Assigned.

10.2 This method was revised in 1978 as a combination of withdrawn methods TAPPI T 439 and TAPPI T

a revision was completed in 1997; the method was made classical in 2015.

10.2.1 The qualitative method was referred to TAPPI T 421.

10.2.2 The colorimetric quantitative procedure was deleted from the body of the method and is now reported in the Appendix. The colorimetric method was primarily recommended for low titanium contents and is less versatile and precise than the volumetric method.

10.2.3 This revision recommends the use of dissolving solution for putting the test specimens into solution rather than the separate addition of ammonium sulfate and sulfuric acid. This solution facilitates the solvating of difficult test specimens.

10.2.4 Note 2 in former method T 439 suggesting the addition of excess ferric ammonium sulfate to the reduced titanium solution has been dropped because any iron in the test specimen will be in the ferrous state and will cause high results when this excess ferrous iron is titrated with standardized potassium dichromate. This procedure is suitable for titanium dioxide pigments where the iron content is negligible, but even then it is necessary to run a blank on the aluminum foil since the highest purity foil contains sufficient iron to cause high results. The blank results should be subtracted from the apparent titration. If this is neglected, the results could be high by about 0.5 to 0.7 mL of titrant.

10.2.5 This revision suggests (Note 2) a sodium peroxide fusion for paper samples high in siliceous matter which are difficult to solvate by other means. It is also satisfactory for paper coating solids and for ores and minerals of unknown composition.

Appendix A. Colorimetric method

A.1 Scope

A.1.1 This method describes a procedure for the colorimetric quantitative determination of titanium dioxide (TiO_2) in paper and other materials (2).

A.1.2 This method is only suitable when the amount of TiO_2 in the ash is less than 0.01 g or when the paper has a high filler content other than TiO_2 .

A.2 Summary

A.2.1 The titanium in dilute H_2SO_4 solution is combined with H_2O_2 and the resulting yellow to brownish orange complex is measured spectrophotometrically.

A.3 Apparatus

A.3.1 *Spectrophotometer*, or other instrument for accurately measuring the light transmission of a solution, at 420 nm.

A.3.2 *Ashing equipment*, a silica, or preferably a platinum, dish and a muffle furnace at $925 \pm 25^\circ\text{C}$.

A.3.3 *Other apparatus*: 5, 10, 15, 20, 25, and 30 mL volumetric pipettes; one 200 and six 100 mL volumetric flasks; 25 and 100 mL graduated cylinders; 250 mL beaker; hot plate.

A.4 *Calibration*. Calibrate the photometric apparatus as follows: dissolve the equivalent of 0.1 g of TiO_2 in the standard sample in 10 g of $(\text{NH}_4)_2\text{SO}_4$ and 35 mL of concentrated H_2SO_4 . Add 90 mL of water; filter and wash through a fine paper into a 200 mL volumetric flask. Cool, dilute to volume, and mix. One mL of this solution contains 0.0005 g of TiO_2 . Transfer aliquots of 5, 10, 15, 20, 25, and 30 mL respectively, to 100 mL volumetric flasks and add 20 mL of 1:1 H_2SO_4 to each portion. Add 15 mL of 3% H_2O_2 , dilute to volume, mix, and measure the transmittance at 420 nm preferably in a 5 mm cell. Plot the transmittance versus the concentration of TiO_2 . Draw a curve through the plotted points. Check at least one point on the curve prior to a test to ensure that the characteristics of the photometer have not changed.

A.5 Reagents

A.5.1 *Hydrochloric acid*, concentrated HCl.

A.5.2 *Dissolving solution*

A.5.2.1 *Ammonium sulfate*, $(\text{NH}_4)_2\text{SO}_4$.

A.5.2.2 *Sulfuric acid*, concentrated H_2SO_4 .

A.5.2.3 Heat together 100 g of ammonium sulfate and 180 mL of concentrated sulfuric acid until the salt is dissolved and light fumes appear. Cool and store in a glass stoppered bottle.

A.5.3 *Standard titanium dioxide*, obtainable from the NIST, with analysis.

A.5.4 *Hydrogen peroxide*, 3% H_2O_2 . Dilute 10 mL of reagent grade 30% H_2O_2 to 100 mL with distilled water. This solution is sufficiently stable for 5 days.

A.6 Procedure**A.6.1 For paper**

A.6.1.1 Determine the moisture content of the paper according to T 412.

A.6.1.2 Ash the paper at $925 \pm 25^\circ\text{C}$ in a clean dish or crucible. Weigh the ash to obtain the percentage, then accurately weigh and place in a 250 mL beaker a portion of ash containing not more than 0.01 g of TiO_2 . Proceed to A.6.3

NOTE 5: If only the percentage of TiO_2 in the paper, and not the proportionate amount in the ash is required, ash one or more grams of the paper in a platinum crucible and transfer the ash quantitatively to the 250 mL beaker.

A.6.2 *Other specimens.* Accurately weigh out a specimen containing not over 0.01 g of TiO_2 . If moisture or organic material is present, first dry the specimen and then ignite to constant weight at dull red heat. Transfer quantitatively to a 250 mL beaker. Proceed to A.6.3.

A.6.3 Add 20 mL of dissolving solution. Heat on a hot plate until white SO_3 fumes are evolved; then continue the heating strongly until solution is complete (usually requires not over 5 min of boiling) or it is apparent that the residue is composed of siliceous matter. Cool, and cautiously add 50 mL of water.

A.6.3.1 If insoluble matter is present, filter through fine filter paper, and wash with 5 mL of distilled water.

NOTE 6: To completely dissolve the specimen, fuse it in a platinum crucible with 8 g of anhydrous Na_2CO_3 for 1 h at 900°C . Cool, and place the crucible and contents in a 250 mL beaker, and add 40 mL of water and 25 mL 1:1 concentrated H_2SO_4 . When the specimen is dissolved, remove the crucible and cover.

A.6.3.2 Transfer clear solution to a 100-mL volumetric flask, add 15 mL of 3% H_2O_2 , dilute to volume, and mix. The color develops immediately.

A.6.4 Fill the photometer cell and measure the light transmittance to 420 nm.

NOTE 7: The photometer reading should be obtained within one hour of color development.

A.7 Interpretation of photometer reading

A.7.1 Obtain the titanium dioxide content from the calibration curve developed in A.4.

A.8 *Report.* The average of three tests make up a test result.

A.8.1 Report the percentage of TiO_2 in the paper on the moisture free weight to the nearest 0.1%.

A.8.2 Report the percentage of TiO_2 in other materials on an "as received" basis.

A.9 Precision

A.9.1 In paper ash based on limited experience.

A.9.1.1 Repeatability (within a laboratory) = at 5% level, 5.63%; at 50% level, 8.79%; at 60% level, 6.17%.

A.9.1.2 Reproducibility (between laboratories) = not known.

A.9.1.3 Comparability (between materials) = not known; in accordance with the definition of these terms in T 1200.

Literature cited

1. Rahm, J. A., *Anal. Chem.* 24 (11): 1832 (1952).
2. Griffin, R. C., "Technical Methods of Analysis," 2nd Ed., McGraw Hill, New York, 1927, p. 778.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department.

