Ti-Pure®

TITANIUM DIOXIDE

DETERMINATION OF SLURRY SOLIDS

METHOD: T4400.570.01.WP
I. Principle

Percent solids of titanium dioxide slurry is determined by evaporating the water and weighing the residue. Two methods are employed to dry the titanium dioxide slurries depending upon the character of the slurry. The methods are conventional convection oven and the newer microwave oven.

II. Applicability

This method applies to the determination of percent solids in titanium dioxide slurries.

III. Limitations

The method measures all material which does not evaporate in the test as titanium dioxide. In addition, the percent solids of some slurries measured by the microwave method does not agree with the ASTM method and the convection oven method must be used. The percent solids of any new grade of "Ti-Pure" slurry must be measured by the ASTM method until the accuracy of the microwave method is verified on that slurry.

IV. Sensitivity, Precision and Accuracy

A. Sensitivity

The data are not available.

B. Precision

1. Single Operator

   The average analysis (\(\bar{X}\)), standard deviation (s) and 95% confidence limits (95% CL) established for the single operator precision of the method were as follows:
<table>
<thead>
<tr>
<th>% Solids</th>
<th>71.37</th>
<th>0.04</th>
<th>+ 0.08</th>
</tr>
</thead>
</table>

The above data were calculated from eight replicate analyses of one sample performed by one technician over a period of a few days using the Labwave 9000 microwave method.

2. Multiple Operator

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

<table>
<thead>
<tr>
<th>% Solids</th>
<th>71.39</th>
<th>0.05</th>
<th>+ 0.10</th>
</tr>
</thead>
</table>

The above data were calculated from 66 replicate analyses of one sample performed by four technicians over a period of 10 days using the Labwave 9000 microwave method.

<table>
<thead>
<tr>
<th>% Solids</th>
<th>76.59</th>
<th>0.16</th>
<th>± 0.029</th>
</tr>
</thead>
</table>

The above data were calculated from 115 replicate analyses of one sample of R-942 slurry, performed by six technicians over a period of several days using the CEM LABWAVE 9000 at 80% power.

C. Accuracy

Appendix 2 contains a tabulation of a comparison of Percent Solids by the ASTM method (oven drying) and the Microwave method. There is no known standard for direct comparison but the comparison between the microwave method and the accepted ASTM method is generally excellent.

Appendix 5 contains a table showing recent data (7/00) that compares the results of various grades by the Convection oven and microwave method. The Microwave test were performed on CEM Labwave 9000 at
different settings, i.e. 40% and 80% power. Agreement between the Convection oven and Microwave tests was determined to be a function of power setting.

V. Special Apparatus (Equivalent apparatus may be substituted)

1. Microwave Method

   a. Microwave Moisture/Solids Analyzer, Model AVC-80, CEM Corp., P.O. Box 200, Mathewa, NC 28106-0200, Tel: (800) 726-3331.

   b. Microwave Moisture/Solids Analyzer, Model Labwave 9000, CEM Corp. (Alternate to above).

   c. Microwave Moisture/Solids Analyzer, Model SS-5 (Smart System 5), CEM Corp. (alternate to above).

   d. Glass fiber sample pads, reorder #20-20015, same supplier. (No substitutes.)

   e. Desiccator.

   f. A laboratory roll mill with speed suitable for keeping a slurry sample mixed or for remixing a sample that has settled.

   g. A 3 mL disposable syringe or a pipette suitable for delivering 3 mL of slurry or 2 to 5 mL disposable droppers.

2. Convection Oven Method

   a. Convection oven, capable of sustained operation at 110 ± 5°C.

   b. Disposable aluminum pans, approximately 60-mm diameter by 18-mm high, 1 to 2 grams in weight.

   c. Analytical balance accurate to 0.1 mg.

   d. Desiccator.

   e. A 3 mL disposable syringe or a pipette suitable for delivering 3 mL of slurry or 2 to 5 mL disposable droppers.
VI. Reagents

1. Indicating drying medium.

VII. Special Safety Considerations

A. Product Hazards

No product hazards have been identified. 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. For more information, consult MSDS No. 2816CR.

B. Procedure Hazards

1. Microwave Oven Method

a. The microwave oven utilizes high voltages and microwave radiation in its operation. Instrument service and repair should be undertaken only by those skilled in high voltage and microwave power system maintenance. Operation of this instrument should not be attempted if there is damage to the oven enclosure, the oven door or its seals. Do not operate this instrument with any object placed between the oven front face and the door, and do not allow any type of residue to accumulate on the door sealing surfaces. Do not attempt to operate this instrument with the door open since open-door operation can result in harmful exposure to microwave energy. Do not tamper with or defeat the door safety interlock system.

b. Do not place metal in the microwave.

c. Have a trained representative from the Safety Office (or other qualified individual) inspect the microwave oven for microwave leaks. Details of this procedure can be found in Appendix 3.

d. Do not slam microwave oven door.

2. Convection Oven Method

a. Care should be taken with this oven as with any hot equipment.
VIII. Procedure

A. Operating Conditions

1. Microwave Oven Method

   This instrument can be operated in either of two modes:

   Mode #1 - The Auto Time - uses the weigh-dry-weigh technique or a specific time of exposure selected by the operator.

   Mode #2 – The Auto Stop - which monitors the drying curve and automatically stops the test when a constant weight has been achieved. This mode is used in this method.

   Note: When using the CEM LABWAVE 9000, follow manufactures equipment manual for operation of the equipment.

2. Convection Oven Method

   110 ± 5°C for 60 to 65 minutes.

B. Calibration

   The Microwave oven needs routine calibration. The power or temperature settings on the Microwave ovens should be adjusted to maintain acceptable calibration. Generally, the Microwave oven method should be calibrated against the Convection oven to within +/- 0.05 % (absolute) on a monthly basis, but local site practices/procedures apply.

   Before making a calibration change, it is necessary to check the microwave drying system, computer, and balance for proper operation. These procedures are described in detail in the manufacturer's operating manuals.

C. Sampling

   1. Normally, samples are supplied by manufacturing. Samples of slurries should be tested promptly as changes can occur in properties on standing. In addition, slurries should be shaken before testing to assure homogeneity.

   2. If sample has settled for a long period of time, place it on a roll mill for an hour minimum before running percent solids.
D. Sample Analysis

1. Microwave Oven Method

A. AVC-80 Microwave Oven Method

If the AVC-80 is off, press the orange POWER switch upwards to turn on the unit. The switch button will illuminate, several beep tones will be sounded, and the display will show:

SELECT MODE M= .

(If the AVC-80 is already on and has been operating in another mode, press: CLEAR)

Press 2 followed by READY. The display will show:

% MOISTURE will be displayed.

Since % Solids are desired as the final result, press CHANGE. The display will now show:

% SOLIDS WILL BE DISPLAYED.

PRESS READY, AND THE DISPLAY WILL SHOW:

SET POWER P= %.

FOR THE INITIAL RUN PRESS 1,0,0, FOLLOWED BY READY to enter 100% power into the computer memory. The display will now show:

SET TIME-INTERVAL DT= SEC.

This request is for one of the drying curve slope parameters. It is the time interval in which the sample's weight loss (to be selected in the next step), is equal to or less than the selected amount which will cause the test to be terminated and the result to be computed. Any time from 0 to 99 seconds may be entered, but for the initial run press 1, 0, READY to enter 10 seconds into the computer memory. The display will show:

SET WEIGHT-DIFFERENTIAL DW= mg.
This request is for the value of weight loss occurring in the previously selected time interval which will terminate the test. For the initial run, press 2, READY. The display will show:

\[ \text{WEIGHT 0.4064 GMS P=100\% T=00.00} \]

(WEIGHT value displayed is approximate.)

Select two sample pads. Form one pad into a shallow cup by placing one pad over a Falcon cup lid and pressing down with a half pint lid without tearing the pad. Open the drying system door, lift the air shield, place the pads on the balance pan with the pressed pad on the bottom, and close the door. Press TARE. The display will show a WEIGHT reading and a

\[ \text{WAIT} \]

message indicating the weight measuring system and computer are seeking a stable weight measurement. In a few seconds, the display will show:

\[ \text{WEIGHT 0.0000 GMS P=100\% T=00.00} \]

indicating that the weight of the pads, balance stem and pan have been tared to zero.

Open the door, remove the top pad, pipette 3 mL of slurry onto the bottom pad, cover with the second pad, and close the door.

Press RUN. The display will show an increasing WEIGHT reading with a

\[ *\ldots\text{WAIT}\.\ldots* \]

message, as above, indicating the system is seeking the maximum value of the initial sample weight before starting to dry the sample. This will be followed in a few seconds by the display of the sample WEIGHT and the POWER and TIME settings.

When the preselected endpoint is reached, the beep tone will sound, the LED RUN indicator will go out, the result will be displayed as follows with this example:

\[ 70.54\% \text{ SOLIDS P = 100\% TIME = 02.06 MINUTES} \]
Press READY to begin the next test.

1. Microwave Oven Method

B. Labwave 9000 Microwave Oven Method

Set up and operation of the Labwave 9000 is analogous to the AVC-80 as described above. Program set-up parameters are given below.

1. The Auto-stop or Constant Weight mode must be selected.

2. Computer must be set-up to report results as % solids

3. Time Interval = 10 seconds (a longer interval may be used, but not shorter).

4. Weight Differential = 2mg

5. Maximum drying time = 7 minutes (suggested, not critical)

6. Power setting varies according to calibration, typically 40-80 %.

1. Microwave Oven Method

C. Operation of the Smart System-5

NOTE: The microwave should be left on at all times. If the microwave is switch off for an extending period of time, ensure that the microwave warm-up for at least 45 minutes prior to use.

CEM MAIN MENU (Always press EXIT to return to MAIN MENU)

1. QUICK TEST
2. EDIT/CREATE METHOD
3. LOAD METHOD
4. SETUP
5. PRINT
6. STATISTIC

1. Press 3 on keyboard (LOAD METHOD).
2. Select test from Load Method menu.

   1. 941
   2. 746, 942

   NOTE: Main menu screen is displayed and the test select will appear near the bottom of display.

3. Press READY.

4. Open door and put two pads on balance then close door. Insure the door is closed.

5. Press TARE (unit will beep and return to solids display screen).

6. Put sample between pads using a syringe (2 - 2.5 cc's).

7. Press START (unit will beep and print solids results when complete).

8. Repeat steps 1-7 for next sample.

   NOTE: If power outage occurs, restart unit, wait for main menu to appear, then press READY to continue.

SETUP

1. Power: 100 %
2. Delta Weight: 0.5 mg
3. Delta Time: 10 Seconds
4. Max Time: 10 Minutes
5. Bias: + 0.00 %
6. Max Temp.: 110 Degrees C

2. Convection Oven Method

   With a plastic spoon, transfer approximately 10 g of slurry to a tared aluminum weighing dish.

   Weigh rapidly on an analytical balance to 4 decimal places.
Place weighing dish and slurry in an oven (not forced air) for 1 hour ± 5 minutes at 110 ± 5°C.

Remove from the oven and place dish in a desiccator until cool.

Remove from the desiccator and weigh rapidly to 4 decimal places.

2A. Convection Oven Method (ASTM Procedure)

Weigh two new, empty aluminum dishes each to 0.1 mg (4 decimal places) for each dish. (This is W1).

With a syringe add 2 mL of distilled water to each dish.

Shake or stir the slurry sample until it is homogeneous and free of any settled material. Insert a spatula or the like to make sure there is no settled material.

Immediately withdraw 0.4 to 0.8 g of slurry in a new, empty disposable syringe or dropper. The specified amount can be estimated by a prior trial in another syringe or dropper. Wipe off the slurry from the outside of the syringe or dropper with a clean, absorbent paper. Cover sample bottle.

Weigh the syringe or dropper, containing the slurry, on an analytical balance, to 0.1 mg (4 decimal places) (This is W2).

Transfer the contents of the syringe or dropper into one of the weighed aluminum dishes. Add the slurry dropwise, gently shaking the dish to disperse the test slurry in the water. When no additional slurry can be transferred from the syringe or dropper, reweigh the syringe or dropper with any residual material inside, to 0.1 mg (4 decimal places) (This is W3).

Shake sample again briefly and follow the above procedure for the second aluminum dish.
Place the two dishes and contents directly onto the metal shelf in the gravity convection oven at 105 ± 2°C for 60 to 65 minutes. (Do not dry in the oven for longer than the specified 65 minutes).

Remove the dishes from the oven, using tongs or gloves, and cool in a desiccator for 10 to 60 minutes. (Do not cool longer than 60 minutes since there is a slight possibility of an equilibrium moisture exchange between the drying medium and some dried titanium dioxide pigments).

Remove one dish at a time, from the desiccator, and weigh immediately on an analytical balance to 0.1 mg (4 decimal places) (This is W4 for each dish).

E. Calculations

1. Microwave Oven Method

   No calculation necessary.

2. Convection Oven Method

   The formula to be used to calculate percent solids is as follows:

   \[
   \text{% Solids} = \frac{\text{Weight of dry solids} \times 100}{\text{Weight of Slurry}}
   \]

   For instance:

   \[
   \begin{align*}
   \text{Weight of slurry} & = 9.2715 \text{ g} \\
   \text{Weight of dry solids} & = 7.1932 \text{ g}
   \end{align*}
   \]

   \[
   \begin{align*}
   \text{7.1932} & \times 100 \\
   \frac{100}{9.2715} & = 77.58\%
   \end{align*}
   \]
The formula to be used to calculate percent solids is as follows:

\[
\frac{(W4 - W1)100}{W2 - W3}
\]

Where:

- \(W1\) = Weight of empty aluminum dish, g
- \(W2\) = Weight of syringe or dropper plus slurry, g
- \(W3\) = Weight of syringe or dropper after slurry has been discharged into aluminum dish, g
- \(W4\) = Weight of dish and slurry after drying, g

Example:

- \(W1 = 1.4431\)
- \(W2 = 2.0894\)
- \(W3 = 1.4905\)
- \(W4 = 1.8158\)

\[
\frac{(1.8158 - 1.4431)100}{2.0894 - 1.4905} = 62.23
\]

Calculate the mean value of duplicate measurements to two decimal places.

Round the calculated mean value to the nearest 0.1% and report as percent solids. This rounded mean value is considered to be one result

Example: 62.2%

IX. Quality Control

Calibration checks are made per individual site calibration procedures and schedules.
X. Comments

If the sample pads are removed from the microwave oven to add the slurry sample, the results tend to be less reproducible than the method described in this method due to evaporation of water before the sample is weighed.

XI. References

1. ASTM D3926 - 80 (Reapproved 1987).

2. MSDS No. 2816CR for Titanium Dioxide.


XII. Appendix

1. Microwave Leakage Measurements.

2. Summary of Recent Correlation Data and Statistics.

The information set forth herein is furnished free of charge and is based on technical data that DuPont believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. Since conditions of use are outside our control, we make no warranties, express or implied, and assume no liability in connection with any use of this information. Nothing herein is to be taken as a license to operate under or a recommendation to infringe any patents.
The AVC-80 door and cavity assembly provides the tightest containment of microwave energy of any microwave oven/drying system on the market today. The door and cavity are extremely durable, designed for reliable operation under the most severe plant and laboratory conditions. External radiation tests are performed on the AVC-80 at various points in the manufacturing process with the result that leakage from the finished instrument is only a fraction of that allowed by U.S. law.

It is recommended, however, that periodic (as required by site safety regulations) microwave leakage measurements be made by the user to insure that the containment has not been breached through damage to the door seal/cavity assembly or debris lodged in the door seal itself.

Close the drying system door and put the instrument in a drying mode at 100% power. Measure the microwave leakage around the door seal, at the cabinet louvers, and at the openings in the rear cover of the instrument using an appropriate microwave survey meter such as a Holaday Industries Model HI-1500 (available from CEM Corporation). The U.S. Dept. of Health and Human Services (HHS) defines excessive leakage as 1 mw/cm² or more for new microwave ovens and 5 mw/cm² or greater for used ovens. The AVC-80 will show no more that 0.5 mw/cm² of leakage and will not leak more than this during its lifetime. This is the maximum leakage level allow by CEM for the AVC-80; however, the leakage from a typical AVC-80 will be much less than this maximum level.

If, however, this measurement shows leakage to be above 1 mw/cm² do not attempt further operation of the system. Call CEM Corporation for instructions.