

TITANIUM DIOXIDE

Prepared at the 67th JECFA (2006) and published in FAO JECFA Monographs 3 (2006), superseding specifications prepared at the 63rd JECFA (2004) and published in FNP 52 Add 12 (2004) and in the Combined Compendium of Food Additive Specifications, FAO JECFA Monographs 1 (2005). An ADI “not limited” was established at the 13th JECFA (1969).

SYNONYMS

Titania, CI Pigment white 6, CI (1975) No. 77891, INS No. 171

DEFINITION

Titanium dioxide is produced by either the sulfate or the chloride process. Processing conditions determine the form (anatase or rutile structure) of the final product.

In the sulfate process, sulfuric acid is used to digest ilmenite (FeTiO_3) or ilmenite and titanium slag. After a series of purification steps, the isolated titanium dioxide is finally washed with water, calcined, and micronized.

In the chloride process, chlorine gas is reacted with a titanium-containing mineral under reducing conditions to form anhydrous titanium tetrachloride, which is subsequently purified and converted to titanium dioxide either by direct thermal oxidation or by reaction with steam in the vapour phase. Alternatively, concentrated hydrochloric acid can be reacted with the titanium-containing mineral to form a solution of titanium tetrachloride, which is then further purified and converted to titanium dioxide by hydrolysis. The titanium dioxide is filtered, washed, and calcined.

Commercial titanium dioxide may be coated with small amounts of alumina and/or silica to improve the technological properties of the product.

C.A.S. number	13463-67-7
Chemical formula	TiO_2
Formula weight	79.88
Assay	Not less than 99.0% on the dried basis (on an aluminium oxide and silicon dioxide-free basis)

DESCRIPTION

White to slightly coloured powder

FUNCTIONAL USES

Colour

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4) Insoluble in water, hydrochloric acid, dilute sulfuric acid, and organic solvents. Dissolves slowly in hydrofluoric acid and hot concentrated sulfuric acid.

Colour reaction Add 5 ml sulfuric acid to 0.5 g of the sample, heat gently until fumes of sulfuric acid appear, then cool. Cautiously dilute to about 100 ml with water and filter. To 5 ml of this clear filtrate, add a few drops of hydrogen peroxide; an orange-red colour appears immediately.

PURITY

Loss on drying (Vol. 4) Not more than 0.5% (105°, 3 h)

Loss on ignition (Vol. 4) Not more than 1.0% (800°) on the dried basis

Aluminium oxide and/or silicon dioxide Not more than 2%, either singly or combined
See descriptions under TESTS

Acid-soluble substances Not more than 0.5%; Not more than 1.5% for products containing alumina or silica.
Suspend 5 g of the sample in 100 ml 0.5 N hydrochloric acid and place on a steam bath for 30 min with occasional stirring. Filter through a Gooch crucible fitted with a glass fibre filter paper. Wash with three 10-ml portions of 0.5 N hydrochloric acid, evaporate the combined filtrate and washings to dryness, and ignite at a dull red heat to constant weight.

Water-soluble matter (Vol. 4) Not more than 0.5%
Proceed as directed under acid-soluble substances (above), using water in place of 0.5 N hydrochloric acid.

Impurities soluble in 0.5 N hydrochloric acid

Antimony Not more than 2 mg/kg
See description under TESTS

Arsenic Not more than 1 mg/kg
See description under TESTS

Cadmium Not more than 1 mg/kg
See description under TESTS

Lead Not more than 10 mg/kg
See description under TESTS

Mercury (Vol. 4) Not more than 1 mg/kg

Determine using the cold vapour atomic absorption technique. Select a sample size appropriate to the specified level

TESTS

PURITY TESTS

Impurities soluble in 0.5 N hydrochloric acid

Antimony, arsenic, cadmium and lead
(Vol.4)

Transfer 10.0 g of sample into a 250-ml beaker, add 50 ml of 0.5 N hydrochloric acid, cover with a watch glass, and heat to boiling on a hot plate. Boil gently for 15 min, pour the slurry into a 100- to 150-ml centrifuge bottle, and centrifuge for 10 to 15 min, or until undissolved material settles. Decant the supernatant extract through a Whatman No. 4 filter paper, or equivalent, collecting the filtrate in a 100-ml volumetric flask and retaining as much as possible of the undissolved material in the centrifuge bottle. Add 10 ml of hot water to the original beaker, washing off the watch glass with the water, and pour the contents into the centrifuge bottle. Form a slurry, using a glass stirring rod, and centrifuge. Decant through the same filter paper, and collect the washings in the volumetric flask containing the initial extract. Repeat the entire washing process two more times. Finally, wash the filter paper with 10 to 15 ml of hot water. Cool the contents of the flask to room temperature, dilute to volume with water, and mix.

Determine antimony, cadmium, and lead using an AAS/ICP-AES technique appropriate to the specified level. Determine arsenic using the ICP-AES/AAS-hydride technique. Alternatively, determine arsenic using Method II of the Arsenic Limit Test, taking 3 g of the sample rather than 1 g. The selection of sample size and method of sample preparation may be based on the principles of the methods described in Volume 4.

Aluminium oxide

Reagents and sample solutions

0.01 N Zinc Sulfate

Dissolve 2.9 g of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in sufficient water to make 1000 ml. Standardize the solution as follows: Dissolve 500 mg of high-purity (99.9%) aluminium wire, accurately weighed, in 20 ml of concentrated hydrochloric acid, heating gently to effect solution, then transfer the solution into a 1000-ml volumetric flask, dilute to volume with water, and mix. Transfer a 10 ml aliquot of this solution into a 500 ml Erlenmeyer flask containing 90 ml of water and 3 ml of concentrated hydrochloric acid, add 1 drop of methyl orange TS and 25 ml of 0.02 M disodium ethylenediaminetetraacetate (EDTA). Add, dropwise, ammonia solution (1 in 5) until the colour is just completely changed from red to orange-yellow. Then, add:

- (a): 10 ml of ammonium acetate buffer solution (77 g of ammonium acetate plus 10 ml of glacial acetic acid, dilute to 1000 ml with water) and
- (b): 10 ml of diammonium hydrogen phosphate solution (150 g

of diammonium hydrogen phosphate in 700 ml of water, adjusted to pH 5.5 with a 1 in 2 solution of hydrochloric acid, then dilute to 1000 ml with water).

Boil the solution for 5 min, cool it quickly to room temperature in a stream of running water, add 3 drops of xylene orange TS, and mix.

Using the zinc sulfate solution as titrant, titrate the solution to the first yellow-brown or pink end-point colour that persists for 5-10 sec. (*Note:* This titration should be performed quickly near the end-point by adding rapidly 0.2 ml increments of the titrant until the first colour change occurs; although the colour will fade in 5-10 sec, it is the true end-point. Failure to observe the first colour change will result in an incorrect titration. The fading end-point does not occur at the second end-point.)

Add 2 g of sodium fluoride, boil the mixture for 2-5 min, and cool in a stream of running water. Titrate this solution, using the zinc sulfate solution as titrant, to the same fugitive yellow-brown or pink end-point as described above.

Calculate the titre T of zinc sulfate solution by the formula:

$$T = 18.896 W / V$$

where

T is the mass (mg) of Al_2O_3 per ml of zinc sulfate solution

W is the mass (g) of aluminium wire

V is the ml of the zinc sulfate solution consumed in the second titration

$$18.896 = (R \times 1000 \text{ mg/g} \times 10 \text{ ml/2})/1000 \text{ ml and}$$

R is the ratio of the formula weight of aluminium oxide to that of elemental aluminium.

Sample Solution A

Accurately weigh 1 g of the sample and transfer to a 250-ml high-silica glass Erlenmeyer flask. Add 10 g of sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$). (*Note:* Do not use more sodium bisulfate than specified, as an excess concentration of salt will interfere with the EDTA titration later on in the procedure.) Begin heating the flask at low heat on a hot plate, and then gradually raise the temperature until full heat is reached. (*Caution:* perform this procedure in a well ventilated area.) When spattering has stopped and light fumes of SO_3 appear, heat in the full flame of a Meeker burner, with the flask tilted so that the fusion of the sample and sodium bisulfate is concentrated at one end of the flask. Swirl constantly until the melt is clear (except for silica content), but guard against prolonged heating to avoid precipitation of titanium dioxide. Cool, add 25 ml sulfuric acid solution (1 in 2), and heat until the mass has dissolved and a clear solution results. Cool, and dilute to 120 ml with water. Introduce a magnetic stir bar into the flask.

Sample Solution B

Prepare 200 ml of an approximately 6.25 M solution of sodium

hydroxide. Add 65 ml of this solution to Sample Solution A, while stirring with the magnetic stirrer; pour the remaining 135 ml of the alkali solution into a 500-ml volumetric flask.

Slowly, with constant stirring, add the sample mixture to the alkali solution in the 500-ml volumetric flask; dilute to volume with water, and mix. (*Note:* If the procedure is delayed at this point for more than 2 hours, store the contents of the volumetric flask in a polyethylene bottle.) Allow most of the precipitate to settle (or centrifuge for 5 min), then filter the supernatant liquid through a very fine filter paper. Label the filtrate Sample Solution B.

Sample Solution C

Transfer 100 ml of the Sample Solution B into a 500-ml Erlenmeyer flask, add 1 drop of methyl orange TS, acidify with hydrochloric acid solution (1 in 2), and then add about 3 ml in excess. Add 25 ml of 0.02 M disodium EDTA, and mix. [*Note:* If the approximate Al_2O_3 content is known, calculate the optimum volume of EDTA solution to be added by the formula: $(4 \times \% \text{Al}_2\text{O}_3) + 5$.]

Add, dropwise, ammonia solution (1 in 5) until the colour is just completely changed from red to orange-yellow. Then add 10 ml each of *Solutions 1* and *2* (see above) and boil for 5 min. Cool quickly to room temperature in a stream of running water, add 3 drops of xylenol orange TS, and mix. If the solution is purple, yellow-brown, or pink, bring the pH to 5.3 - 5.7 by the addition of acetic acid. At the desired pH, a pink colour indicates that not enough of the EDTA solution has been added, in which case, discard the solution and repeat this procedure with another 100 ml of Sample Solution B, using 50 ml, rather than 25 ml, of 0.02 M disodium EDTA.

Procedure

Using the standardized zinc sulfate solution as titrant, titrate Sample Solution C to the first yellow-brown or pink end-point that persists for 5-10 sec. (*Important:* See Note under "*0.01 Zinc sulfate*"). This first titration should require more than 8 ml of titrant, but for more accurate work a titration of 10-15 ml is desirable.

Add 2 g of sodium fluoride to the titration flask, boil the mixture for 2-5 min, and cool in a stream of running water. Titrate this solution, using the standardized zinc sulfate solution as titrant, to the same fugitive yellow-brown or pink end-point as described above.

Calculation:

Calculate the percentage of aluminium oxide (Al_2O_3) in the sample taken by the formula:

$$\% \text{Al}_2\text{O}_3 = 100 \times (0.005VT)/S$$

where

V is the number of ml of 0.01 N zinc sulfate consumed in

the second titration,
T is the titre of the zinc sulfate solution,
S is the mass (g) of the sample taken, and
 $0.005 = 500 \text{ ml} / (1000\text{mg/g} \times 100 \text{ ml})$.

Silicon dioxide

Accurately weigh 1 g of the sample and transfer to a 250-ml high-silica glass Erlenmeyer flask. Add 10 g of sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$). Heat gently over a Meeker burner, while swirling the flask, until decomposition and fusion are complete and the melt is clear, except for the silica content, and then cool. (*Caution:* Do not overheat the contents of the flask at the beginning, and heat cautiously during fusion to avoid spattering.)

To the cooled melt add 25 ml of sulfuric acid solution (1 in 2) and heat carefully and slowly until the melt is dissolved. Cool, and carefully add 150 ml of water by pouring very small portions down the sides of the flask, with frequent swirling to avoid over-heating and spattering. Allow the contents of the flask to cool, and filter through fine ashless filter paper, using a 60 degree gravity funnel. Rinse out all the silica from the flask onto the filter paper with sulfuric acid solution (1 in 10). Transfer the filter paper and its contents into a platinum crucible, dry in an oven at 120° , and heat the partly covered crucible over a Bunsen burner. To prevent flaming of the filter paper, first heat the cover from above, and then the crucible from below.

When the filter paper is consumed, transfer the crucible to a muffle furnace and ignite at 1000° for 30 min. Cool in a desiccator, and weigh. Add 2 drops of sulfuric acid (1 in 2) and 5 ml of concentrated hydrofluoric acid (sp.gr. 1.15), and carefully evaporate to dryness, first on a low-heat hot plate (to remove the HF) and then over a Bunsen burner (to remove the H_2SO_4). Take precautions to avoid spattering, especially after removal of the HF. Ignite at 1000° for 10 min, cool in a desiccator, and weigh again. Record the difference between the two weights as the content of SiO_2 in the sample.

METHOD OF ASSAY

Accurately weigh about 150 mg of the sample, previously dried at 105° for 3 hours, and transfer into a 500-ml conical flask. Add 5 ml of water and shake until a homogeneous, milky suspension is obtained. Add 30 ml of sulfuric acid and 12 g of ammonium sulfate, and mix. Initially heat gently, then heat strongly until a clear solution is obtained. Cool, then cautiously dilute with 120 ml of water and 40 ml of hydrochloric acid, and stir. Add 3 g of aluminium metal, and immediately insert a rubber stopper fitted with a U-shaped glass tube while immersing the other end of the U-tube into a saturated solution of sodium bicarbonate contained in a 500-ml wide-mouth bottle, and generate hydrogen. Allow to stand for a few minutes after the aluminium metal has dissolved completely to produce a transparent purple solution. Cool to below 50° in running water, and remove the rubber stopper carrying the U-tube. Add 3 ml of a saturated potassium thiocyanate solution as an indicator, and immediately titrate with 0.2 N ferric ammonium sulfate until a faint brown colour that persists for 30

seconds is obtained. Perform a blank determination and make any necessary correction. Each ml of 0.2 N ferric ammonium sulfate is equivalent to 7.990 mg of TiO_2 .