TITANIUM DIOXIDE

Prepared at the 63rd JECFA (2004), published in FNP 52 Add 12 (2004) superseding specifications prepared at the 39th JECFA (1992), published in FNP 52 Add 1 (1992). An ADI "not limited" was established at the 13th JECFA (1969). Heavy metals and arsenic specifications revised at the 59th JECFA (2002)

SYNONYMS Titanium dioxide, CI Pigment white 6, CI (1975) No. 77891, INS No. 171

DEFINITION Titanium dioxide consists essentially of pure titanium dioxide which may be coated with small amounts of alumina and/or silica to improve the technological properties of the product. It is manufactured by digesting ilmenite ($FeTiO_3$) or ilmenite and titanium slag with sulfuric acid and the product is diluted with water or dilute acid. The resulting liquor is clarified by sedimentation to remove insoluble residues such as silica and iron is removed by crystallization (as $FeSO_4$. $7H_2O$) and filtration. The liquid is then hydrolyzed with alkali under controlled conditions to produce a precipitate of titanium dioxide. The product is filtered, washed, calcined and micronized.

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 Amorphous white 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 fume of sulfuric acid appear, then cool. Cautiously dilute to about 100 ml with water and filter. To 5 ml of this clear filtrate, add 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 dried basis

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

Acid-soluble substances

Not more than 0.5%
Not more than 1.5% for products containing alumina and/or silica.
Suspend 5 g of the sample in 100 ml 0.5 N hydrochloric acid and on 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 (Vol. 4)

Not more than 3 mg/kg (Method II)
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 an atomic absorption technique appropriate to the specified level. The selection of samples size and method of sample preparation may be based on principles of methods described in Volume 4, "Instrumental Methods".

TESTS

PURITY TESTS

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, then 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 slurry 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 atomic absorption technique appropriate to the specified level and arsenic using Method II of Volume 4.

Aluminium oxide

Reagents and sample solutions
0.01 N Zinc sulfate: Dissolve 2.9 g of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) 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 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), and continue as directed below under Sample Solution C, beginning with "Add dropwise ammonia solution (1 in 5) until...".

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

$$T = \frac{18.896 \times W}{V}$$

where

T = mg of Al_2O_3 per ml of zinc sulfate solution
W = g of the aluminium wire
V = ml of the zinc sulfate solution consumed in the second titration
18.896 factor derived as follows:

$$\frac{MW\ of\ Al_2O_3}{MW\ of\ Al} \times 1000\ mg/kg \times 10\ ml/2$$

Sample Solution A
Fuse 1 g of the sample, accurately weighed, with 10 g of sodium bisulfate ($NaHSO_4 \cdot H_2O$) contained in a 250-ml high-silica glass Erlenmeyer flask. (Caution: 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 at low heat on a hot plate, then gradually raise the temperature until full heat is reached. When spattering has stopped and light fumes of SO_3 appear, heat in the full flame of a Meker burner, with the flask tilted so that the fusion is concentrated at one end of the flask. Swirl constantly until the melt is clear (except for silica content), but guarding against prolonged heating to avoid precipitation of titanium dioxide. Cool, add 25 ml sulfuric acid solution (1 in 2) and then heat until the mass has dissolved and a clear solution results. Cool, and dilute to 120 ml with water.

Sample Solution B
Measure out 200 ml of approximately 6.25 M sodium hydroxide, and add 65 ml of it to Sample Solution A while stirring with a magnetic stirrer ; pour the remaining 135 ml of the alkali solution into a 500-ml volumetric flask.

Slowly, and with constant stirring, add the sample mixture to the alkali solution in the 500-ml volumetric flask, then 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 out (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 ethylenediamine tetraacetate, 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 x % Al_2O_3) + 5.]
Add, dropwise, ammonia solution (1 in 5) until the colour is just completely changed from red to orange-yellow, the add 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 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 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 another 100 ml of Sample Solution B should be taken and treated as directed from the beginning of the description of "Sample Solution C", except that 50 ml, rather than 25 ml, of 0.02 M disodium ethylenediamine tetraacetate should be used.

Procedure
Titrate Sample Solution C with 0.01 N zinc sulfate to the first yellow-brown or pink end-point colour that persists for 5-10 sec.

Caution:
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. 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, boil the mixture for 2-5 min, and cool in a stream of running water. Titrate the EDTA (which is released by fluoride from its aluminium complex) with 0.01 N zinc sulfate 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:

$$\%\ of\ Al_2O_3 = \frac{V\,x\,T}{2\,x\,S}$$

where

V = ml of 0.01 N zinc sulfate consumed in the second titration
T = the titer of the zinc sulfate solution, determined previously
S = g of the sample taken

Silicon dioxide

Fuse 1 g of the sample, accurately weighed, with 10 g of sodium bisulfate ($NaHSO_4 \cdot H_2O$) contained in a 250-ml high-silica glass Erlenmeyer flask. Heat gently over a Meker 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 cold melt add 25 ml of sulfuric acid solution (1 in 2), and heat very carefully and very slowly until the melt is dissolved. Cool, and carefully add 150 ml of water, 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 then filter through fine ashless filter paper, using a 60 degree gravity funnel. Wash 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 120^0, and then heat the partly covered crucible over a Bunsen burner. To prevent flaming of the filter paper, heat first 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^o 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^o 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

Transfer about 300 mg of the sample, previously dried at 105^o for 3 h and accurately weighed, into a 250-ml beaker, add 20 ml of sulfuric acid and 7 to 8 g of ammonium sulfate, and mix. Heat on a hot plate until fumes of sulfuric acid appear, and continue heating over a strong flame until the sample dissolves or it is apparent that the undissolved residue is siliceous matter. Cool, cautiously dilute with 100 ml of water, and stir. Heat carefully to boiling while stirring, allow the insoluble matter to settle, and filter. Transfer the entire residue to the filter, and wash thoroughly with cold dilute sulfuric acid TS. Dilute the filtrate with water to 200 ml, and cautiously add about 10 ml of stronger ammonia TS to reduce the acid concentration to about 5% by volume of sulfuric acid.

Prepare a zinc amalgam Jones reductor column in a 25 cm glass tube, placing a pledget of glass wool in the bottom of the tube and filling the constricted portion of the tube with zinc amalgam prepared as follows:

Add to 30 mesh zinc to a 2% mercuric chloride solution, using about 10 min, 100 ml of the solution for each 100 g of zinc. After about 10 min, decant the solution from the zinc, the wash the zinc with water by decantation. Transfer the zinc amalgam to the reductor tube, wash the column with 100-ml portions of dilute sulfuric acid TS until 100 ml of the washing does not decolourize 1 drop of 0.1 N potassium permanganate.

Place 50 ml of ferric ammonium sulfate TS in a 500-ml suction flask, and add 0.1 N potassium permanganate until a faint pink colour persists for 5 min. Attach the Jones reductor tube containing the Zinc amalgam column to the neck of the flask, and pass 50 ml of dilute sulfuric acid TS through the tube at a rate of about 30 ml per min. Pass the prepared titanium solution through the column at the same rate, followed by 100

ml each of dilute sulfuric acid TS and water. During these operations, keep the tube filled with solution or water above the upper level of the amalgam column. Gradually release the suction, wash down the outlet tube and the sides of the receiver, and titrate immediately with 0.1 N potassium permanganate. Perform a blank determination, substituting 200 ml of dilute sulfuric acid (1 in 20) for the sample solution, and make any necessary correction. Each ml of 0.1 N potassium permanganate is equivalent to 7.990 mg of TiO_2.