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भारतीय मानक
स्पेक्ट्रोफोटोमेट्रिक द्वारा कठोर धातु में टाइटेनियम का
निर्धारण - पद्धति
(आई एस 12483 का पहला पुनरीक्षण)

Draft Indian Standard
DETERMINATION OF TITANIUM IN HARDMETALS BY
SPECTROPHOTOMETRIC - METHOD

(First Revision of IS 12483)

ICS 77.160

Powder Metallurgical Materials and Products
Sectional Committee, MTD 25

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FOREWORD

(Formal clauses to be added later)

This standard was first published in 1988. This revision has been brought out to bring the standard in the latest style and format of the Indian Standards.

In addition, a major change has been incorporated in 7.3.1, '800 °C' is substituted by '80 °C'.

In the preparation of this standard, assistance has been derived from ISO 4501 : 1978 'Hardmetals - Determination of titanium - Photometric peroxide method'.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'. The number of significant places retained in the rounded off value should be same as that of the specified value in this standard.

Draft Indian Standard

**DETERMINATION OF TITANIUM IN HARDMETALS BY
SPECTROPHOTOMETRIC METHOD**

(First Revision of IS 12483)

1 SCOPE

1.1 This standard covers a spectrophotometric method for the determination of the titanium content in carbides and hardmetals.

1.2 This method is applicable to the following having titanium content exceeding 0.2 percent (m/m):

- a) Carbides and binder metal powder mixtures, free of lubricant; and
- b) All grades of pre sintered or sintered hardmetals.

2 PRINCIPLE

Formation of a yellow complex of pertitanic acid. Determination of the absorbance of the complex.

3 INTERFERING ELEMENTS

The effect of interfering elements which also form coloured complexes with hydrogen peroxide under the conditions specified, for example vanadium and molybdenum shall be taken into account. A correction can be applied if the content is below 5 percent of each.

4 REAGENTS

During the analysis, use only reagents of analytical grade, and distilled water or water of equivalent purity.

4.1 Ammonium Hydrogen Fluoride

4.2 Ammonium Sulphate

4.3 Sodium Disulphite

4.4 High Purity Titanium Metal or Titanium Dioxide

4.5 Citric Acid Solution - 30 percent (m/m).

4.6 Perchloric Acid - $\rho = 1.54$ or 1.67 g/ml.

4.7 Concentrated Sulphuric Acid - $\rho = 1.84$ g/ml.

4.8 Dilute Sulphuric Acid - $\rho = 1.54$ g/ml (concentrated sulphuric acid, $\rho = 1.84$ g/ml, diluted 1 + 1).

4.9 Hydrogen Peroxide - 30 percent (m/m).

4.10 Hydrofluoric Acid - $\rho = 1.12$ g/ml.

4.11 Concentrated Nitric Acid - $\rho = 1.42$ g/ml.

5 APPARATUS

5.1 Ordinary Laboratory Apparatus

5.2 Spectrophotometer or Filter Photometer

6 SAMPLE PREPARATION

6.1 The sample shall be crushed to a powder in a mortar made of a material which does not alter the sample composition. The powder shall pass through a 180 µm sieve.

NOTE - For sintered hardmetals, the preparation of sample may be as agreed to between the purchaser and the manufacturer.

6.2 The analysis shall be carried out on at least two test portions.

7 PROCEDURE

7.1 Select the mass of the test portion, the volume of the volumetric flask and the cell length in accordance with Table 1.

TABLE 1 TEST PORTION, FLASK VOLUME AND CELL LENGTH (Clause 7.1)				
SI No.	Titanium Content, Percent (m/m)	Test Portion, Mass (m)	Flask Volume (ml)	Cell Length (mm)
i)	0.2 to 4	0.2	250	20
ii)	2 to 8	0.2	250	10
iii)	5 to 15	0.2	500	10
iv)	10 to 30	0.1	500	10

NOTE — Approximately 17 mg of titanium in 250 ml of final solution gives unit absorbance with a 10 mm cell.

7.2 Test Portion

Weigh (to the nearest 0.000 1 g) 0.1 g or 0.2 g of the test sample.

7.3 Dissolution

Transfer the test portion into a 100 ml to 200 ml conical flask or a 250 ml beaker. Add 5 g ammonium sulphate and 10 ml concentrated sulphuric acid. Cover the beaker or flask with a watch glass. Heat to boiling until complete dissolution is achieved.

7.3.1 Alternative dissolution method

Transfer the test portion into a platinum dish. Add 10 ml of water and 5 ml of hydrofluoric acid. Cover the dish with a polypropylene or platinum cover. Heat to approximately 80 °C. Add the concentrated nitric acid drop by drop until dissolution is complete. Cool, add 10 ml of concentrated sulphuric acid (4.7) and 5 g of ammonium sulphate. Heat until fumes of SO₃ are observed, and cool again.

7.3.2 If any undissolved particles or carbonaceous matter are left, cool to below 100 °C, and cautiously add 1 ml of per chloric acid. Heat to fume off the perchloric acid, then cool to room temperature.

CAUTION: When using perchloric acid, avoid contact with organic matter.

7.4 Preparation of the Solution for Analysis

Add, in small portions, 1 ml of hydrogen peroxide, mix by shaking. Add, in small portions, 30 ml of citric acid solution while mixing. Add 40 ml of water.

7.4.1 Using a 250 ml volumetric flask

Transfer the solution into 250 ml volumetric flask, rinsing copiously with water. Add 25 ml of dilute sulphuric acid (1 : 1) (4.8), fill nearly to the mark and mix. Cool, add 1 ml hydrogen peroxide, mix, make up to volume and mix again.

7.4.2 Using a 500 ml volumetric flask

Transfer the solution into 500 ml volumetric flask, rinsing copiously with water. Add 30 ml citric acid solution and 50 ml dilute sulphuric acid (1: 1) (4.8), fill nearly to the mark and mix. Cool, add 2 ml hydrogen peroxide, mix, make up to volume and mix again.

7.5 Compensating Solution

Transfer approximately 30 ml of the coloured solution (7.4) into a 50 ml beaker. Add approximately 0.2 g of sodium disulphide to decolourize the solution. If necessary, repeat the addition of sodium disulphate.

7.6 Determination of Absorbance

Choose appropriate cells. Measure the absorbance of the coloured and the compensating solutions at a wavelength of 420 nm using the same cell or a matched pair of cells.

8 Elimination of Interference

8.1 Vanadium

Transfer 30 ml of the coloured solution (7.4) into a 50 ml beaker and add approximately 0.1 g ammonium hydrogen fluoride, which destroys the coloured titanium complex. Wait for 3 min. The colour left is due to vanadium.

8.1.1 Measure the absorbance and subtract it from the absorbance due to titanium plus vanadium.

8.2 Molybdenum

The colour of the molybdenum peroxide complex is weak. It cannot be compensated for chemically but correction can be calculated from the molybdenum content. 1 percent of molybdenum in the sample corresponds to approximately 0.08 percent of titanium at 420 nm, but the correction should be determined with the spectrophotometer used.

9 Preparation of the Calibration Curve

9.1 Standard Titanium Solution

The standard titanium solution can be prepared from titanium metal or titanium dioxide.

9.1.1 Standard titanium solution from titanium metal

Weigh approximately 250 mg of the titanium metal (4.4) and transfer it into a 200 ml conical flask. Add 30 ml water and 20 ml sulphuric acid (1 : 1) (4.8). Cover the flask. Warm gently and keep the volume constant by adding water until all metal has dissolved. Cool and add approximately 1 ml hydrogen peroxide oxidize the titanium. Evaporate the water by heating to fumes. Cool, add 10 g ammonium sulphate and heat gently until deposits on the walls flask have dissolved. Cool and add about 50 ml of water, transfer into a 250 ml volumetric flask and add 25 ml dilute sulphuric acid (1 : 1) (4.8). Cool, make up to volume with water and mix. Calculate the titanium content in grams of titanium per litre.

9.1.2 Standard titanium solution from titanium dioxide

Weigh a quantity of the titanium dioxide calculated to contain approximately 250 mg of titanium and transfer it into a 200 ml conical flask. Add 10 g ammonium sulphate and 10 ml concentrated sulphuric acid. Cover the flask. Heat to near boiling until a clear solution is obtained. Cool, add, in small portions, 1 ml hydrogen peroxide while mixing by shaking. Add about 50 ml water, transfer into a 250 ml volumetric flask and add 25 ml dilute sulphuric acid (1 : 1) (4.8). Cool, make up to volume with water and mix. Calculate the titanium content in grams of titanium per litre.

9.2 Calibration

Determine the slope of the absorbance titanium curve, that is the absorbance for 1.0 mg of titanium per 250 ml of solution, for example, as follows:

Into four conical flasks, transfer 5 g ammonium sulphate and 10 ml concentrated sulphuric acid. Add separately to three of the flasks 5.0 ml, 10.0 ml and 15.0 ml standard titanium solution. Use the remaining flask for the blank test. Continue as in 7.4 to 7.6.

10 Test Results

10.1 Calculation

The titanium content, expressed as a percentage by mass, is given by the formula

$$\text{Titanium content (percent by mass)} = \frac{100 \times A \times V}{25 \times a \times m \times L}$$

where

A = absorbance from the titanium in the hardmetal;

a = absorbance when the concentration is 1 mg of titanium per 250 ml with a 10 mm cell;

m = mass, in mg, of the test portion;

V = volume, in ml, of the coloured solution; and

L = cell length, in mm.

NOTE - The result shall be rounded to the nearest 0.01 percent.

10.2 Tolerances

The deviations between two or three independent determinations shall not exceed the values shown in Table 2

TABLE 2 PERMISSIBLE DEVIATION (Clause 10.2)			
SI No.	Titanium Content, <i>percent</i>	Range for two determinations, <i>percent</i>	Range for three determination, <i>percent</i>
(1)	(2)	(3)	(4)
i)	From 0.2 to 5	0.10	0.12
ii)	Over 5 to 8	0.15	0.18
iii)	Over 8 to 15	0.20	0.25
iv)	Over 15	0.30	0.35

10.3 Final Results

The Final result shall be reported as given follows:

- a) Reference to this Indian Standard IS 12483;
- b) Report the arithmetical mean of acceptable determinations rounded to the nearest 0.1 percent;
- c) All details necessary for identification of the test sample;
- d) Result obtained; and
- e) Details of any occurrence which may have affected the result.