

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Determination of
Oxygen in Titanium and
Titanium Alloys**

JIS H 1620—1989

Translated and Published

by

Japanese Standards Association

Printed in Japan

In the event of any doubt arising,
the original Standard in Japanese is to be final authority.

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Methods for Determination of Oxygen in
Titanium and Titanium Alloys

H 1620-1989

1. Scope

This Japanese Industrial Standard specifies the methods for determination of oxygen in titanium and titanium alloys.

Remark: The units given in { } in this Standard are based on the International System of Units (SI) and are appended for informative reference.

Further, the traditional units and units by SI with { } thereafter in this Standard shall be converted on January 1, 1991 to units specified in Appendix.

2. General Matters

General matters common to the analytical methods are in accordance with JIS H 1611 and JIS Z 2613.

3. Classification of Determination Methods

The methods for determination of oxygen shall be in accordance with any one of the following methods.

- (1) Vacuum Melting - Constant Volume Manometric Method This method applies to the sample of 0.005 wt % or over to and excluding 0.5 wt % in oxygen content.
- (2) Vacuum Melting - Gas Chromatography This method applies to the sample of 0.005 wt % or over to and excluding 0.5 wt % in oxygen content.
- (3) Inert Gas Melting - Coulometric Method This method applies to the sample of 0.005 wt % or over to and excluding 0.5 wt % in oxygen content.
- (4) Inert Gas Melting - Gas Chromatography This method applies to the sample of 0.005 wt % or over to and excluding 0.5 wt % in oxygen content.
- (5) Inert Gas Melting - Infrared Absorption Method This method applies to the sample of 0.005 wt % or over to and excluding 0.5 wt % in oxygen content.

Applicable Standards:

JIS H 1611-General Rule for Chemical Analysis of Titanium

JIS Z 2613-General Rules for Determination of Oxygen in Metallic Materials

4. Vacuum Melting - Constant Volume Manometric Method

4.1 Purport Use a graphite crucible in a vacuum, melt a sample together with platinum by a high frequency induction heating system, extract oxygen as carbon monoxide together with other gases, collect in a definite volume, and measure the pressure. Heat carbon monoxide in the collected gas and hydrogen extracted at the same time, respectively make them carbon dioxide and water with copper (II) oxide, and absorb water in diphosphorus pentoxide. Thereafter, measure the pressure. Then, cool carbon dioxide with liquid nitrogen. After solidification, measure the pressure.

4.2 Materials and Reagents The materials and reagents shall be in accordance with 6.1.2 (3) to (7) of JIS Z 2613 and otherwise, shall be as follows.

(1) Platinum The preparation shall be in accordance with 5.2 (1) of JIS Z 2613. However, acetone is used for a washing solvent.

4.3 Apparatus For the apparatus, a gas extraction part of 3.2.1 (2) (2-1) of JIS Z 2613 and a gas analysis part of 3.3.1 (2) of JIS Z 2613 are connected to be used (see Fig. 13 of JIS Z 2613).

4.4 Weighing Out Amount of Sample A sample shall be weighed out in accordance with Table 1 to the nearest 1 mg.

Table 1. Weighing Out Amount of Sample

Oxygen content wt %	Weighing out amount of sample g
0.005 or over to and excl. 0.05	0.30
0.05 or over to and excl. 0.5	0.10

4.5 Operation

4.5.1 Preparatory Operation The operation shall be performed in accordance with the procedure of 6.1.3 (1) to 6.1.4 (1) of JIS Z 2613. However, a degassing temperature of a graphite crucible and others shall be 2200 to 2300°C. Further, not less than 10 times amount of total mass of a sample of platinum [4.2 (1)] shall be used as a bath metal, and the metal bath shall be prepared at a temperature slightly higher than a gas extraction temperature.

4.5.2 Determining Operation Successively to the preparatory operation, the operation shall be performed in accordance with the procedure of 6.1.4 (3) of JIS Z 2613. However, the gas extraction temperature shall be 1930 to 1970°C.

4.6 Blank Test The blank test shall be in accordance with 6.1.4 (2) of JIS Z 2613. However, the sample is not projected.

4.7 Calculation The calculation shall be in accordance with 6.1.4 (4) of JIS Z 2613. However, conversion coefficient shall be preliminarily calculated in accordance with 6.1.4 (5) of JIS Z 2613.

5. Vacuum Melting - Gas Chromatography

5.1 Purport Use a graphite crucible in a vacuum, melt a sample together with platinum by heating with a high frequency induction heating system, and extract oxygen as carbon monoxide together with other gases. After collecting the extracted gas in a gas burette by using a Toepler pump, pass the collected gas through a separation column, separate carbon monoxide from other gases, conduct it to a heat conductivity detector, and measure the variation of heat conductivity by carbon monoxide.

5.2 Materials and Reagents The materials and reagents shall be in accordance with 3.2.1 (1) of JIS Z 2613 and otherwise shall be as follows.

- (1) Platinum The platinum shall be as described in 4.2 (1).
- (2) Helium Helium of not less than 99.99 vol %
- (3) Carbon monoxide Carbon monoxide of not less than 99.5 vol %
- (4) Synthetic zeolite Type A - calcium salt (for instance, molecular sieve 5 A) of 355 to 250 μm (40 to 60 mesh equivalent)

5.3 Apparatus For the apparatus, a gas collecting mercury ejector pump, a gas collecting Toepler pump, a gas burette, and a gas chromatograph of 3.3.6 of JIS 2613 are successively connected to a gas extraction part of 3.2.1 (2) (2-1) of JIS Z 2613. However, the gas chromatograph equipped with a separation column packed with synthetic zeolite [5.2 (4)] and a heat conductivity detector shall be used. An example of the apparatus is given in Attached Fig. 1.

5.4 Weighing Out Amount of Sample A sample shall be weighed out in accordance with Table 2 to the nearest 1 mg.

Table 2. Weighing Out Amount of Sample

Oxygen content wt %	Weighing out amount of sample g
0.005 or over to and excl. 0.20	0.30
0.20 or over to and excl. 0.5	0.10

5.5 Operation

5.5.1 Preparatory Operation The preparatory operation shall be carried out in accordance with the following procedures:

- (1) Operate in accordance with the procedure of 6.1.3 (1) of JIS Z 2613. However, use not less than 10 times the amount of total mass of a sample of platinum [5.2 (1)] as a bath metal.
- (2) Close all cocks, operate an oil rotary pump (T), quietly open a cock C_1 , and exhaust gas for about 5 min. Thereafter, operate a high frequency oscillator, heat a graphite crucible (i) at a degassing temperature of 2200 to 2300°C and perform degassing.
- (3) When the indication of a Pirani vacuum gauge (k) becomes almost constant, operate a gas extracting mercury diffusion pump (m) and a gas collecting mercury ejector pump (n), open a cock C_2 , close the cock C_1 , and continue to degas for about 3 h.
- (4) At about 1 h before end of degassing, cause helium [5.2 (2)] to flow by 30 ml per min from a helium cylinder (He), turn on a power source of a gas chromatograph, and establish a temperature of a constant temperature bath at 50°C.
- (5) Open a cock C_6 on conduction side to the gas chromatograph, and successively open cocks C_8 and C_9 . When mercury of a gas collecting Toepler pump (o) has completely risen in a gas burette (p), close the cock C_8 . Then, open a cock C_5 . When the surface of mercury in the gas burette (p) reaches the inlet of a cock C_6 by lifting a mercury leveling bulb (r), close the cock C_6 , return the mercury leveling bottle (r) to an original position, and close the cock C_5 .
- (6) Close the cock C_9 , open a cock C_7 to a gas exhaust system side connected to an oil rotary pump (T), and exhaust gas for about 5 min. Thereafter, close the cock C_7 , and keep a carbon monoxide gas holder (q) under vacuum.
- (7) Adjust a temperature of the graphite crucible (i) at a gas extraction temperature of 1930 to 1970°C, close the cock C_2 , and open a cock C_3 and the cock C_8 .
- (8) Alternately open and close the cock C_9 and a cock C_{10} , repeat the operation in which mercury of the gas collecting Toepler pump (o) is raised and lowered for about 15 min, and collect the extracted gas in the gas burette (p). Thereafter, close the cock C_8 .
- (9) Open the cock C_5 , open the cock C_6 on conduction side of the gas chromatograph with operating the mercury leveling bulb (r), and conduct the gas collected in the gas burette (p) into the gas chromatograph. Thereafter, close the cocks C_6 and C_5 , and measure the peak area of the gas chromatogram of carbon monoxide.
- (10) Open the cock C_8 , and repeat the operations of (8) and (9) until the peak height of the gas chromatogram of carbon monoxide reaches not more than 5 mm (¹).
- (11) Keep the temperature of the graphite crucible at a temperature slightly higher than a gas extraction temperature. After projecting platinum into the graphite crucible, repeat the operation of (8) to (10), and measure the peak area of the gas chromatogram of carbon monoxide finally obtained.

Note ⁽¹⁾ The sensitivity of a recorder is so regulated that the peak height per 20 μ l of carbon monoxide in standard state becomes about 5 mm.

5.5.2 Determining Operation Successively to the preparatory operation, the determining operation shall be carried out in accordance with the following procedures:

- (1) Keep a platinum bath in a graphite crucible (i) at a gas extraction temperature of 1930 to 1970°C.
- (2) Project a sample, and immediately open a cock C₈. Thereafter, operate in accordance with the procedures of (8) and (9) of 5.5.1.

5.6 Blank Test Take the peak area measured in 5.5.1 (11) as the peak area of a blank test.

5.7 Preparation of Working Curve A working curve shall be prepared in accordance with the following procedures:

- (1) Open a cock C₇, fill a carbon monoxide holder (q) by carbon monoxide [5.2 (3)] from a carbon monoxide cylinder (CO), and close the cock C₇.
- (2) Open a cock C₈ to the carbon monoxide holder (q) side, open a cock C₅, operate a mercury leveling bulb (r), take carbon monoxide into a gas burette (p), and close the cock C₆. Thereafter, operate the mercury leveling bulb (r), and measure the volume of carbon monoxide. At the same time, measure the atmospheric pressure and room temperature.
- (3) Open the cock C₆ on the introduction side to a gas chromatograph, operate the mercury leveling bulb (r), introduce the carbon monoxide in the gas burette (p) into the gas chromatograph, close the cocks C₆ and C₅, and measure the peak area of the gas chromatogram of carbon monoxide.
- (4) Repeat the operation of (2) and (3) so that the amount of carbon monoxide introduced into the gas chromatograph becomes stepwise.
- (5) Convert the volume of carbon monoxide introduced into the gas chromatograph to the mass of oxygen from the following formula (apply this provision until Dec. 31, 1990).

$$\text{Mass of oxygen (g)} = \frac{15.9994 \times P \times V}{6.236 \times 10^4 \times (273 + t)}$$

where P : atmospheric pressure measured in (2) (mmHg) {kPa}
[However, for the International System of Units (SI), the part of 6.236×10^4 shall be converted to 8.314×10^3 .]

V : volume of carbon monoxide taken into the gas burette in (2) (ml)

t : room temperature measured in (2) (°C)

- (6) Prepare the relation curve between the mass of oxygen introduced into the gas chromatograph and the peak area, parallel transfer the relation curve so as to pass through the origin, and take it as the working curve.

5.8 Calculation Obtain the mass of oxygen from the peak area obtained in 5.5.2 (2) and 5.6 and the working curve prepared in 5.7, and calculate the content of oxygen in the sample from the following formula.

$$\text{Oxygen content wt \%} = \frac{A_1 - A_2}{m} \times 100$$

where, A_1 : mass of oxygen obtained from the peak area of 5.5.2 (2) (g)

A_2 : mass of oxygen obtained from the peak area of 5.6 (g)

m : weighing out amount of sample (g)

6. Inert Gas Melting - Coulometric Method

6.1 Purport Use a graphite crucible in a current of argon, melt a sample by heating, and oxidize the gas extracted from the sample to carbon dioxide by passing diiodine pentaoxide. Thereafter, absorb it in weak alkaline barium perchlorate solution which is adjusted at a definite pH, and measure the quantity of electricity required for returning the pH decreased by absorption to original pH by electrolysis of the barium perchlorate solution.

6.2 Materials and Reagents The materials and reagents shall be as follows:

- (1) Platinum Platinum shall be as specified in 4.2 (1)
- (2) Tin (granular)
- (3) Iron Iron shall be as specified in 5.2 (3) of JIS Z 2613
- (4) Nickel Nickel of not more than 0.005 wt % in oxygen content
- (5) Argon Argon of not less than 99.99 vol %
- (6) Sodium chloride
- (7) Barium perchlorate
- (8) Barium carbonate
- (9) 2-Propanol
- (10) Graphite crucible A graphite crucible conforming to an impulse furnace. An example thereof is given in Attached Fig. 3.