

JIS

JAPANESE INDUSTRIAL STANDARD

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

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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
Zirconium and Zirconium Alloys

H 1665-1988

1. Scope

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

2. General Matters

General matters common to the methods for chemical analysis shall be in accordance with JIS H 1650 and JIS Z 2613.

3. Classification of Methods

The method for determination of oxygen shall be in accordance with either one of the following methods:

- (1) Vacuum Fusion - Constant Volume Monometric Method This method applies to the sample of 0.005 wt % and over to 0.2 wt % excl. in oxygen content.
- (2) Inert Gas Fusion - Gas Chromatography This method applies to the sample of 0.005 wt % and over to 0.2 wt % excl. in oxygen content.
- (3) Inert Gas Fusion - Infrared Absorption Method This method applies to the sample of 0.005 wt % and over to 0.2 wt % excl. in oxygen content.

4. Preparation of Sample

A sample shall be prepared in accordance with 4.4.1 (1) of JIS Z 2613 or chemical polishing. In the case of execution of chemical polishing, after dipping a sample into the mixed solution of 100 ml nitric acid (1+1) and 5 ml hydrofluoric acid, it is successively cleaned with water, ethanol, and acetone each one minute by using an ultrasonic cleaner to be dried by sending air.

Applicable Standards:

JIS H 1650-General Rules for Chemical Analysis of Zirconium and
Zirconium Alloys

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

5. Vacuum Fusion - Constant Volume Manometric Method

5.1 Summary A sample together with a bath metal is fused with a graphite crucible by high frequency induction heating system in a vacuum. Oxygen is made carbon monoxide, extracted together with other gases and collected in a fixed volume. Then, the pressure thereof is measured. Carbon monoxide in this collection gas and hydrogen extracted simultaneously are respectively made carbon dioxide and water with heated copper (II) oxide. After absorbing water in diphosphorus pentaoxide, the pressure is measured. Then, after cooling carbon dioxide with liquid nitrogen to be solidified, the pressure is measured.

5.2 Materials and Reagents The materials and reagents shall be as prescribed in 6.1.2 (3) to (7) of JIS Z 2613 and as follows:

(1) Bath Metal Platinum⁽¹⁾

Note ⁽¹⁾ The preparation shall be as prescribed in 5.2 (1) of JIS Z 2613. However, acetone is used as washing solvent.

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

5.4 Weighing-Out Amount of Sample The weighing-out amount of a sample shall be, as a rule, in accordance with Table according to the oxygen content.

Table Weighing-Out Amount of Sample

Oxygen content wt %	Weighing-out amount of sample g
0.005 and over to 0.05 excl.	0.30
0.05 and over to 0.2 excl.	0.10

5.5 Operation

5.5.1 Preparatory Operation The preparatory operation shall be carried out in accordance with the procedures of 6.1.3 (1) to 6.1.4 (1) in JIS Z 2613. However, a degassing temperature for a graphite crucible and others shall be 2200 to 2300°C and not less than 7 times amount of total mass of a sample of platinum [5.2 (1)] shall be used as a bath metal. The bath metal shall be prepared at a temperature slightly higher than a gas extracting temperature.

5.5.2 Determination Operation The determination operation, in succession to the preparatory operation, shall be carried out in accordance with the procedures of 6.1.4 (3) in JIS Z 2613. However, a gas extracting temperature shall be 1950 to 2000°C.

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

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

6. Inert Gas Fusion - Gas Chromatography

6.1 Summary A sample together with a bath metal are heated to be fused by an impulse system by using a graphite crucible in a gas current of helium. Oxygen is made carbon monoxide and extracted together with other gases. Carbon monoxide in the extracted gas is oxidized to carbon dioxide with heated copper (II) oxide and carbon dioxide is separated from other gases with a dehydration tube and a gas separation tube. It is introduced to a heat conductivity detector and the change of heat conductivity due to carbon dioxide is measured.

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

- (1) Bath Metal Platinum⁽²⁾, nickel⁽³⁾, or tin⁽⁴⁾.
- (2) Helium Helium of not less than 99.99 vol %
- (3) Graphite Crucible A graphite crucible complying with an impulse furnace. An example thereof is given in Attached Fig. 1.

Notes (2) The preparation shall be as prescribed in 5.2 (1) of JIS Z 2613. However, a foil of 0.01 to 0.03 mm in thickness is used.

(3) A foil of not more than 0.005 wt % in oxygen content and 0.01 to 0.03 mm in thickness is used. After washing it successively with mixed acid (75 acetic acid, 25 nitric acid, and 2 hydrochloric acid) heated at about 80°C, water, ethanol, and acetone for each 30 seconds, it is dried by sending air.

(4) It is used in the case where platinum-tin or nickel-tin is used as a metal bath. Tin is prepared as described in 5.2 (2) of JIS Z 2613.

6.3 Apparatus⁽⁵⁾ The apparatus is composed of a helium cleaning part, a gas extraction part, a gas separation part, a gas measurement part, etc. An example of the apparatus is given in Attached Fig. 2.

- (1) Helium Cleaning Part The helium cleaning part is composed of a deoxidation tube, a carbon dioxide absorption tube, a dehydration tube, an electric resistance heating furnace, etc.
 - (a) Deoxidation Tube A stainless steel tube packed by metallic copper (granular). It is heated with an electric resistance heating furnace to be used.
 - (b) Carbon Dioxide Absorption Tube A glass tube packed by soda lime, soda asbestos, or sodium hydroxide.
 - (c) Dehydration Tube A glass tube packed by magnesium perchlorate or diphosphorus pentoxide.

Note (5) The structure and use conditions of an apparatus differs according to the apparatus to be used.

- (2) Gas Extraction Part The gas extraction part is composed of a sample projecting device, an impulse furnace, etc.
- (a) Sample Projecting Device A device which can project a sample into an impulse furnace in an inert gas atmosphere.
- (b) Impulse Furnace It is composed of an upper water cooling electrode which is made of copper to be fixed and a lower water cooling electrode which can be vertically moved, of which a graphite crucible [6.2 (3)] pinched between both electrodes can be heated to 2000 to 2500°C in several seconds by application of electric power.
- (3) Gas Separation Part The gas separation part is composed of a dust collection tube, an oxidation tube, a dehydration tube, a separation column, etc.
- (a) Dust Collection Tube A glass tube packed by glass wool.
- (b) Oxidation Tube A glass tube packed by copper (II) oxide. It is heated with an electric resistance heating furnace to be used.
- (c) Dehydration Tube As prescribed in 6.3 (1) (c).
- (d) Separation Column A stainless steel tube or an ethylene tetrafluoride resin tube packed by silica gel.
- (4) Gas Measurement Part The gas measurement part is composed of a heat conductivity detector, an indicating instrument, etc.
- (a) Heat Conductivity Detector It is composed of a contrast cell into which thermistors having uniform characteristics are inserted, a sample cell, etc.
- (b) Indicating Instrument It is an indicating instrument by which a signal based on carbon dioxide detected by a heat conductivity detector.

6.4 Weighing-Out Amount of Sample The weighing-out amount of a sample shall be 0.10 g.

6.5 Operation⁽⁶⁾

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

- (1) After supplying cooling water and helium [6.2 (2)] to an apparatus, turn on the power source. Install each part of the apparatus at specific conditions and stabilize each part of the apparatus.
- (2) Install a new graphite crucible [6.2 (3)] at a specific position, apply power to an impulse furnace and heat the graphite crucible at a degassing temperature⁽⁷⁾.