

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical Analysis
of Calcium-Silicon**

JIS G 1324—1989

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JAPANESE INDUSTRIAL STANDARD

J I S

Methods for Chemical
Analysis of Calcium-Silicon

G 1324-1989

1. Scope

This Japanese Industrial Standard specifies the methods for determination of calcium, silicon, carbon and phosphorus contained in calcium-silicon.

2. General Matters

General matters commonly governing the methods for chemical analysis shall be in accordance with JIS G 1301.

3. Method for Determination of Calcium

3.1 Classification of Determination Methods The determination of calcium shall be in accordance with either of the following methods.

- (1) Potassium Permanganate Titrimetric Method of Precipitated Calcium Oxalate after Iron-Separation This method can be applied to the whole range of calcium content in calcium-silicon.
- (2) Disodium Ethylenediaminetetraacetate Titrimetric Method after Iron-Separation This method can be applied to the whole range of calcium content in calcium-silicon.

3.2 Potassium Permanganate Titrimetric Method of Precipitated Calcium Oxalate after Iron-Separation

3.2.1 Summary Decompose the sample by adding nitric acid and hydrofluoric acid, add perchloric acid, and heat it to generate white fume. After dissolving salts with hydrochloric acid, precipitate and separate iron and the like by neutralizing with aqueous ammonia, and then precipitate calcium oxalate by adding ammonium oxalate. Dissolve this precipitate in sulfuric acid, and titrate the solution with potassium permanganate standard solution.

Applicable Standards:

JIS G 1301-General Rules for Chemical Analysis of Ferroalloys

JIS K 8001-General Rules of Testing Methods for Reagents

JIS Z 2615-General Rules for Determination of Carbon in Metallic Materials

3.2.2 Reagents Reagents shall be as follows.

- (1) Hydrochloric acid (1+1, 1+10)
- (2) Nitric acid (1+1)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Sulfuric acid (1+4)
- (6) Aqueous ammonia (1+1)
- (7) Ammonium chloride
- (8) Ammonium chloride solution Dissolve 20 g of ammonium chloride in 1 l of water, add methyl red solution as an indicator, and then drip aqueous ammonia (1+1) until the solution turns yellow.
- (9) Ammonium oxalate solution (saturated, about 40 g/l)
- (10) Ammonium oxalate solution (5 g/l)
- (11) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4 /l) The methods of preparation, storing and standardization shall be in accordance with 4.4 (9) of JIS K 8001.
- (12) Methyl Red Solution Preparation shall be as shown in 4.3 of JIS K 8001.

3.2.3 Quantity of Sample Weigh out a sample of 0.20 g.3.2.4 Operation

3.2.4.1 Decomposition of Sample Weigh out the sample in a platinum dish (No. 100), add 10 ml of nitric acid (1+1), cover it with a watch glass made of polyethylene or platinum, and decompose it by adding drop by drop about 5 ml of hydrofluoric acid. If this reaction becomes too violent, cool it with water during decomposition. Remove the watch glass while rinsing it with water and, after adding 5 ml of perchloric acid, heat to dryness on a sand bath to generate white fume of perchloric acid. Successively heat it to almost complete dryness. After cooling, add 30 ml of warm hydrochloric acid (1+10) to dissolve soluble salts, and transfer the solution to a beaker (300 ml) while rinsing the dish with water.

3.2.4.2 Separation of Iron or Others Add about 2 g of ammonium chloride and a few drops of the methyl red solution (3.2.2. (12)) as an indicator to the solution obtained in 3.2.4.1, and add bit by bit aqueous ammonia (1+1) while stirring until the solution turns yellow. After boiling it for about 5 min, filtrate the solution through a filter paper (Grade 5 A), and put the filtrate in a beaker (300 ml) to store as a main solution. Wash the precipitate remaining on the filter paper into the former beaker with a

small amount of warm hydrochloric acid (1+10), further wash the paper several times with warm hydrochloric acid (1+10) and then likewise several times with warm water. Put the washings into the beaker already containing the precipitate. After dissolving the precipitate by heating, generate the precipitate as above-mentioned by dripping a few drops of the methyl red solution [3.2.2 (12)] as an indicator, and filtrate it. Wash the precipitate with warm ammonium chloride solution [3.2.2 (8)], and join these washings and filtrate with the main solution.

3.2.4.3 Generation, Filtration and Washing of Precipitate Add hydrochloric acid (1+1) to the solution obtained in 3.2.4.2 until the solution turns red, and heat to concentrate to about 150 ml. Add 20 ml of warm ammonium oxalate solution (saturated), further add bit by bit aqueous ammonia (1+1) while stirring to generate precipitate until the solution turns yellow, heat for about 2 h on a water bath and cool. Filtrate the precipitate through a filter paper (Grade 5 B), and wash it a few times with ammonium oxalate solution (5 g/l) and then wash 5 or 6 times with cold water.

3.2.4.4 Titration Transfer the precipitate obtained in 3.2.4.3 to the former beaker while washing with water, and wash the filter paper first with 25 ml of warm sulfuric acid (1+4) and then about five times with warm water. Put the washings into the former beaker. Dilute the solution with warm water to about 250 ml, heat up to about 80°C and titrate the solution with the 0.02 mol/l potassium permanganate standard solution [3.2.2 (11)] to find the end point when the solution turns pale pink.

3.2.5 Blank Test Carry out the blank test as described in 3.2.4.1 to 3.2.4.4 using only reagents concurrently with the procedures for sample.

3.2.6 Calculation Calculate the calcium content in the sample from the following formula.

$$\text{Calcium wt \%} = \frac{(V_1 - V_2) \times F \times 0.002004}{m} \times 100$$

where, V_1 : consumed volume of 0.02 mol/l potassium permanganate standard solution obtained in 3.2.4.4 (ml)

V_2 : consumed volume of 0.02 mol/l potassium permanganate standard solution obtained in 3.2.5 (ml)

F : factor of 0.02 mol/l potassium permanganate standard solution

m : weighed-out quantity of sample (g)

3.3 Disodium Ethylenediaminetetraacetate Titrimetric Method after Iron-Separation

3.3.1 Summary Decompose the sample with hydrochloric acid and nitric acid, add perchloric acid and heat it to generate white fume. After dissolving the salts in hydrochloric acid, precipitate to eliminate iron and the like by neutralizing with aqueous ammonia, and control its pH with the addition of potassium hydroxide. Add 1-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthol-3-carboxylic acid (hereafter referred to as the "NN") as an indicator, and titrate the solution with disodium ethylenediaminetetraacetate standard solution.

3.3.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid (1+1, 1+10)
- (2) Nitric acid (1+1)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Potassium hydroxide solution (450 g/l)
- (6) Aqueous ammonia (1+1)
- (7) Magnesium hydroxide milk Dissolve 5 g of magnesium chloride hexahydrate in 240 ml of water, add 10 ml of sodium hydroxide solution (200 g/l) and violently agitate this solution into a emulsified state.
- (8) Ammonium chloride
- (9) Ammonium chloride solution (20 g/l) Dissolve 20 g of ammonium chloride in 1 l of water, add the methyl red solution as an indicator, and drip aqueous ammonia until the solution turns yellow.
- (10) Hydroxylammonium chloride solution (60 g/l)
- (11) 0.01 mol/l disodium ethylenediaminetetraacetate (hereafter referred to as "EDTA") standard solution (3.722 g of $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O/l$) The methods of preparation and standardization shall be in accordance with 4.4 (5.3) of JIS K 8001.
- (12) NN indicator Mix 0.2 g of NN and 20 g of potassium nitrate, and grind satisfactorily.
- (13) HNB indicator Mix and grind satisfactorily 0.2 g of sodium 1-(2-hydroxyl-4-sulfo-1-naphthylazo)-2-naphthol-3, 6-disulphonate and 20 g of potassium nitrate.
- (14) Methyl red solution

3.3.3 Weighing out Quantity of Sample The sample of 0.20 g shall be weighed out.

3.3.4 Operation

3.3.4.1 Decomposition of Sample Weigh out the sample into a platinum dish (No. 100), add 10 ml of nitric acid (1+1), cover with a watch glass made of platinum or polyethylene and decompose by adding drop by drop about 5 ml of hydrofluoric acid. If this reaction becomes too violent, cool it with water during decomposition. Remove the watch glass while rinsing it with water, add 5 ml of perchloric acid and heat to dryness on a sand bath to generate white fume of perchloric acid. Successively heat it to almost complete dryness. After cooling, add 30 ml of warm hydrochloric acid (1+10) to dissolve soluble salts, and transfer the solution to a beaker (300 ml) while rinsing the dish with water.

3.3.4.2 Separation of Iron and Others Add about 2 g of ammonium chloride and a few drops of the methyl red solution [3.3.2 (14)] as an indicator to the solution obtained in 3.3.4.1, and add bit by bit aqueous ammonia (1+1) while stirring until the solution turns yellow. After boiling it for about 5 min, filtrate the solution through a filter paper (Grade 5 A), and put the filtrate in a 250-ml volumetric flask to store as a main solution. Wash the precipitate remaining on the filter paper into the former beaker with a small amount of warm hydrochloric acid (1+10), and further wash the paper several times with warm hydrochloric acid (1+10) and then likewise several times with warm water. After dissolving the precipitate by heating, generate the precipitate as above-mentioned by dripping a few drops of the methyl red solution [3.2.2 (12)] as an indicator, and filtrate it. Put the filtrate and washings into the 250-ml volumetric flask already containing the main solution, and wash the precipitate on the filter paper 5 or 6 times with warm ammonium chloride solution [3.3.2 (9)]. After cooling to room temperature, dilute the solution with water up to the marked line.

3.3.4.3 Titration Pipette 25 ml of an aliquot from the solution obtained in 3.3.4.2 into an Erlenmeyer flask (300 ml), dilute it with water up to 50 ml, add 4 ml of potassium hydroxide solution all the while agitating and allow it to stand for 3 or 4 min.

Further add 5 ml of hydroxylammonium chloride solution and about 0.1 g of NN indicator [3.3.2 (12)] or HNB indicator [3.3.2 (13)], and titrate the solution with 0.01 mol/ EDTA standard solution [3.3.2 (11)]. When the color of the solution turns from reddish violet to yellow, add about 4 ml of magnesium hydroxide milk [3.3.2(7)]⁽¹⁾, continue to titrate and take the time when the solution turns blue as the end point.

Note (1) The color change shown at the titration end point becomes more conspicuous by the addition of magnesium hydroxide milk.

3.3.5 Blank Test Carry out the blank test as described in 3.3.4.1 to 3.3.4.3 using only reagents concurrently with procedures for sample.

3.3.6 Calculation Calculate the calcium content in the sample form the following formula.

$$\text{Calcium wt \%} = \frac{(V_1 - V_2) \times F \times 0.0004008}{m \times B} \times 100$$

where, V_1 : consumed volume of 0.01 mol/l EDTA standard solution obtained in 3.3.4.3 (ml)

V_2 : consumed volume of 0.01 mol/l EDTA standard solution obtained in 3.3.5 (ml)

F : factor of 0.01 mol/l EDTA standard solution

m : weighed-out quantity of sample (g)

B : aliquot ratio for sample solution and blank solution

4. Method for Determination of Silicon

4.1 Classification of Determination Methods The methods for determination of silicon shall be in accordance with either of the following methods.

- (1) Silicon Dioxide Gravimetric Method This method can be applied to the whole range of silicon content in calcium silicon.
- (2) Sodium Hydroxide Titrimetric Method after Separation of Precipitated Potassium-Hexafluorosilicate This method can be applied to the whole range of silicon content in calcium-silicon.

4.2 Silicon Dioxide Gravimetric Method

4.2.1 Summary Fuse the sample with fusing mixture or sodium hydroxide, add hydrochloric acid and perchloric acid, and heat it to evaporate to change silicon into insoluble silicic acid. Weigh its weight after igniting the precipitate, treat it with hydrofluoric acid to evaporate silicon dioxide, and then measure its weight.

4.2.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1+1, 1+2, 1+10)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Sulfuric acid (1+1, 1+3)
- (6) Sodium hydroxide
- (7) Fusing mixture [sodium peroxide 2, sodium carbonate (unhydride)1]

(8) Potassium thiocyanate solution (100 g/l)

4.2.3 Quantity of Sample Weigh out 0.20 g of sample.4.2.4 Operation4.2.4.1 Decomposition of Sample The sample shall be decomposed by either of the following methods.

- (1) Case of Fusing with Fusing Mixture Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), adequately mix the sample with 5 g of fusing mixture, and cover the mixed with 1 g of fusing mixture. With a lid on, first heat the crucible at low temperature while rotating it until the inside melts down. Then heat the crucible at about 700°C (dark red) for about 5 min while rotating it to fuse the content completely, and let it cool down. Put the crucible with the lid on in a beaker (500 ml) already containing 60 ml of hydrochloric acid (1+2) to dissolve the fused, and then draw out the crucible and the lid while rinsing with water.
- (2) Case of Fusing with Sodium Hydroxide Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), adequately mix the sample with 5 g of sodium hydroxide, and satisfactorily dehydrate it on a hot plate, cover with a lid, and heat gradually and carefully to fuse the mixed. After cooling, put the crucible and the lid in a polyethylene beaker (300 ml) already containing about 100 ml of warm water to dissolve the fused, and then draw out the crucible and the lid while rinsing with water. After cooling the solution down to room temperature, transfer it into a beaker (500 ml) already containing 20 ml of hydrochloric acid while rinsing with water.

4.2.4.2 Dehydration Treatment of Solicic Acid Add 40 ml of perchloric acid to the solution obtained in 4.2.4.1, and heat the solution to evaporate on a sand bath until white dense fume is generated. Cover it with a watch glass, continue to heat it for about 15 min under the condition that the vapor of perchloric acid is being refluxed along the inside walls of the beaker. After cooling, add 20 ml of hydrochloric acid (1+1) and about 100 ml of warm water to dissolve soluble salts. Remove the watch glass while rinsing it with water, immediately filtrate the solution through a filter paper (Grade 5 A), and put the filtrate into another beaker (500 ml). Remove the precipitate adhering to the inside of the beaker or the watch glass by rubbing with a policeman (rubber-capped glass rod) while rinsing them with warm hydrochloric acid (1+10), transfer them to the tops of the filter paper, and then wash the paper five times with warm hydrochloric acid (1+10) and next with warm water until no iron ion is detected⁽²⁾. Store the precipitate together with the filter paper as the main precipitate.

Note (2) Continue to wash the paper until no (orange) red color is indicated when potassium thiocyanate solution is added to a small quantity of the washings taken.

4.2.4.3 Recovery of Silicon Dioxide Add 10 ml of perchloric acid to the filtrate and washings obtained in 4.2.4.2, and heat to evaporate on a sand bath until white dense fume is generated. Cover with a watch glass, continue to heat for about 15 min under the condition that the vapor of perchloric acid is being refluxed along the inside walls of the beaker. After cooling, add 20 ml of hydrochloric acid (1+1) and about 100 ml of warm water to dissolve soluble salts. Remove the watch glass while rinsing with water, and immediately filtrate the solution through a filter paper (Grade 5 B). Remove the precipitate adhering to the inside of the beaker or the watch glass by rubbing with a policeman while rinsing them with warm hydrochloric acid (1+10), transfer them to the top of the filter paper and then wash the paper five times with warm hydrochloric acid (1+10) and next with warm water until no iron ion is detected⁽²⁾. Discard the filtrate and washings.

4.2.4.4 Ashing and Weighing Ashing and weighing shall be carried out as follows.

- (1) Put two precipitates obtained in 4.2.4.2 and 4.2.4.3 into a platinum crucible (No. 30) together with the filter paper. After drying, heat them gradually until the paper is ashed.
- (2) After strongly heating for about 30 min at about 1100°C, let it cool down to room temperature in a desiccator, and weigh its mass. Repeat this procedure until a constant mass is obtained.

4.2.4.5 Hydrofluoric-acid Treatment and Weighing Hydrofluoric-acid treatment and weighing shall be carried out as follows.

- (1) Moisten the precipitate in the platinum crucible obtained in 4.2.4.4 with a few drops of sulfuric acid (1+3), add 3 to 5 ml of hydrofluoric acid, and heat carefully to dispel silicon dioxide and sulfuric acid.
- (2) After strongly heating for about 30 min at 1100°C, let it cool down to room temperature in a desiccator, and weigh its mass. Repeat this procedure until a constant mass is obtained.

4.2.5 Blank Test Carry out the operations described in 4.2.4.1 to 4.2.4.5 using only reagents concurrently with the procedures for sample.

4.2.6 Calculation Calculate the silicon content in the sample from the following formula.

$$\text{Silicon wt } \% = \frac{[(m_1 - m_2) - (m_3 - m_4)] \times 0.4674}{m_0} \times 100$$

where, m_1 : mass obtained at 4.2.4.4 (2) in sample test (g)

m_2 : mass obtained at 4.2.4.5 (2) in sample test (g)

m_s : mass obtained at 4.2.4.4 (2) in blank test (g)

m_t : mass obtained at 4.2.4.5 (2) in blank test (g)

m_0 : weighed-out quantity of sample (g).

4.3 Sodium Hydroxide Titrimetric Method after Separation of Precipitated Potassium Hexafluorosilicate

4.3.1 Summary Fuse the sample with fusing mixture or sodium hydroxide or potassium hydroxide, dissolve the fused in nitric acid, and precipitate potassium hexafluorosilicate by adding hydrofluoric acid and potassium nitrate. Filter the precipitate, dissolve the filtrate in warm water, and titrate the solution with sodium hydroxide standard solution.

4.3.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid
- (2) Nitric acid (1+1)
- (3) Hydrofluoric acid
- (4) Sodium hydroxide
- (5) Potassium hydroxide
- (6) Fusing mixture [sodium peroxide 1, potassium carbonate (anhydride) 5]
- (7) Potassium nitrate
- (8) Potassium nitrate solution (50 g/l) In case of a showing alkaline property, previously neutralize it with nitric acid.
- (9) 0.5 mol/l sodium hydroxide standard solution (20.0 g NaOH/l) The methods of preparation and standardization shall be as specified in 4.4 (20.2) of JIS K 8001.
- (10) Phenolphthalein solution Dissolve 0.5 g of phenolphthalein in 100 ml of ethanol (95).

4.3.3 Quantity of Sample Weigh out 0.10 g of sample.

4.3.4 Operation

4.3.4.1 Decomposition of Sample and Formation of Precipitate The decomposition of the sample and the formation of precipitate shall be carried out by either of the following.

- (1) Case of Fusing with Fusing Mixture Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), and adequately mix the sample with 3 g of fusing mixture.

With a lid on, first heat the crucible at low temperature while rotating it until the content melts down. Then, heat at about 700°C (dark red) for about 5 min while agitating to fuse the content completely. After cooling, add a small quantity of warm water and gently heat to dissolve the fused. Transfer the solution in a polyethylene beaker (300 ml) already containing 50 ml of nitric acid (1+1) while rinsing the crucible. Add 3 ml of hydrochloric acid to dissolve the fused adhering to its inside walls of the crucible, and satisfactorily wash the crucible and lid with water. Heat this on a water bath to dissolve the fused completely, dilute it with water up to about 80 ml, add 10 ml of hydrofluoric acid and 3 g of potassium nitrate, agitate, and heat the solution for about 15 min on a water bath. Add a bit of filter-paper pulp, and allow to stand for about 30 min while keeping the temperature lower than 15°C to complete the precipitation of potassium hexafluorosilicate.

- (2) Case of Fusing with Alkali Hydroxide Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), and adequately mix the sample with 3 g of sodium hydroxide or potassium hydroxide, and satisfactorily dehydrate on a hot plate, cover with a lid, and heat gradually and carefully to fuse the mixed. After cooling, add a small amount of warm water, and heat gently to dissolve the fused. Transfer the solution to a polyethylene beaker (300 ml) already containing 50 ml of nitric acid (1+1) while rinsing with water. Add 3 ml of hydrochloric acid to dissolve the fused adhering its inside walls of the crucible, and further wash the crucible and lid with water. Heat the beaker on a water bath to completely dissolve the fused and, after diluting the solution to 80 ml with water, add 10 ml of hydrofluoric acid and 3 g of potassium nitrate. Mix them adequately and heat on a water bath for about 15 min. Add a bit of filter-paper pulp, allow to stand for about 30 min while keeping the temperature lower than 15°C to complete the precipitation of potassium hexafluorosilicate.

4.3.4.2 Filtration and Washing Filtrate the precipitate of potassium hexafluorosilicate obtained in 4.3.4.1 through a filter paper (Grade 5 A) on a polyethylene funnel while keeping the temperature of the solution lower than 15°C. Then, repeat washing the precipitate with the potassium nitrate solution kept lower than 15°C until blue litmus paper does not turn red (about 15 times). Transfer the precipitate to an Erlenmeyer flask (200 ml) together with the filter paper, and add about 50 ml of warm water to break the paper to pieces while agitating the solution satisfactorily.

4.3.4.3 Titration After boiling the solution obtained in 4.3.4.2 immediately drip a few drops of phenolphthalein solution [4.3.2 (10)] as an indicator, and add a 0.5 mol/l sodium hydroxide standard solution [4.3.2 (9)] at a stroke nearly to the end point. Then, further add a few drops of phenolphthalein solution [4.3.2 (10)], and titrate the solution with another 0.5 mol/l sodium hydroxide standard solution [4.3.2 (9)] to determine the end point where it turns pale pink.

4.3.5 Blank Test Carry out the operations, described in 4.3.4.1 to 4.3.4.3 using only reagents concurrently with the procedures for sample.

4.3.6 Calculation Calculate the silicon content in the sample from the following formula.

$$\text{Silicon wt \%} = \frac{(V_1 - V_2) \times F \times 0.003511}{m} \times 100$$

where, V_1 : consumed volume of 0.5 mol/l sodium hydroxide standard solution obtained in 4.3.4.3 (ml)

V_2 : consumed volume of 0.5 mol/l sodium hydroxide standard solution obtained in 4.3.5 (ml)

F : factor of 0.5 mol/l sodium hydroxide standard solution

m : weighed-out quantity of sample (g).

5. Methods for Determination of Carbon

5.1 Classification of Methods The methods for determination of carbon shall be in accordance with one of the following.

- (1) Combustion-Gas Volumetric Method This method shall be applied to the sample containing not less than 0.05 wt % of carbon.
- (2) Combustion-Electric Conductivity Method This method shall be applied, when using a tubular electric resistance furnace as a combustion apparatus, to the sample containing not less than 0.005 wt % of carbon; and when using a high-frequency induction furnace, to the sample containing not less than 0.01 wt % of carbon.
- (3) Combustion-Coulometric Method This method shall be applied, when using a tubular electric-resistance furnace as a combustion apparatus, to the sample containing not less than 0.005 wt % of carbon; and when using a high-frequency induction furnace, to the sample containing not less than 0.01 wt % of carbon.
- (4) Combustion-Infrared Ray Absorption Method This method shall be applied, when using a tubular electric-resistance furnace as a combustion apparatus, to the sample containing not less than 0.005 wt % of carbon; and when using a high-frequency induction furnace, to the sample containing not less than 0.01 wt % of carbon.

5.2 Combustion-Gas Volumetric Method

5.2.1 Summary Completely oxidize carbon to change into carbon dioxide by heating the sample in an oxygen-gas flow, and measure the

volume of this carbon dioxide together with oxygen gas after collecting them in a gas burette. Then, eliminate the carbon dioxide by allowing it to be absorbed in an alkaline solution, and then measure the volume of the remaining gas.

5.2.2 Devices and Materials The devices and materials shall be as specified in 5. of JIS Z 2615.

5.2.3 Apparatus The apparatus shall be as specified in 6.3.2 of JIS Z 2615.

5.2.4 Quantity of Sample and Ignition Improver The quantity of the sample shall, as a rule, be as specified in Table. The most suitable ignition improver shall be chosen from those given in 5. (13) of JIS Z 2615, and the improver of an amount most suitable for both the quantity of the sample and the combustion apparatus shall be either adequately mixed with the sample or place all over the sample.

Table. Quantity of Sample

Carbon content wt %	Quantity of sample g
0.05 or over to and excl. 0.3	2.0
0.3 or over	1.0

5.2.5 Operation

5.2.5.1 Preparatory Operation Preparatory operation shall be carried out in accordance with the description in 6.3.3 of JIS Z 2615.

In the case of using a tubular electric-resistance furnace, the temperature inside the tube shall be maintained at 1300 to 1450°C⁽³⁾.

In the case of using a high-frequency induction furnace, the condition needed for running the high-frequency induction furnace shall be established⁽⁴⁾.

Notes ⁽³⁾ This should be corrected with due attention paid to the difference between the temperature indicated on the pyrometer and the one inside the ignition tube.

⁽⁴⁾ This means a condition geared to meet the specifications of the apparatus used, such as anode current, grid current or others of a high-frequency oscillator.

5.2.5.2 Operation for Determination The operation for determination shall be carried out in accordance with either of the following.

- (1) Case of Using a Tubular Electric-Resistance Furnace
Follow the description in 6.3.4 of JIS Z 2615.
- (2) Case of Using a High-Frequency Induction Furnace Follow
the description in Remark to 6.3 of JIS Z 2615.

5.2.6 Blank Test A blank test shall be carried out in accordance with either of the following.

- (1) Case of Using a Tubular Electric-Resistance Furnace
Follow the description in 6.3.5 of JIS Z 2615.
- (2) Case of Using a High-Frequency Induction Furnace Use
the crucible containing no sample but only the same quantity of ignition improver as that added to the sample, and carry out the procedures given in 5.2.5.2 (2).

In the case where use is made of the ignition improver that will generate no induced current by high-frequency current, 0.5 to 1.0 g of the iron or the like of a known and the least possible carbon content shall be used in this procedure, and the blank test value shall be decided on after making a correction of the amount of carbon contained in the added iron.

5.2.7 Calculation Calculate in accordance with the description in 6.3.6 of JIS Z 2615.

5.3 Combustion-Electric Conductivity Method

5.3.1 Summary Completely oxidize carbon to change into carbon dioxide by heating the sample in an oxygen-gas flow, allow it to be absorbed in a specified volume of alkaline solution, and then gauge the change of electric conductivity of the alkaline solution before and after the absorption.

5.3.2 Reagents The reagents shall be as specified in 6.6.2 of JIS Z 2615.

5.3.3 Devices and Materials The devices and materials shall be as specified in 5. of JIS Z 2615.

5.3.4 Apparatus The apparatus shall be as specified in 6.6.3 of JIS Z 2615⁽⁵⁾.

Note ⁽⁵⁾ In place of a tubular electric-resistance furnace, a high-frequency induction furnace may be used. When using a high-frequency induction furnace, such devices as a boat and a boat cover should be replaced by a crucible and a lid.

5.3.5 Quantity of Sample and Ignition Improver The quantity of the sample shall be the one most suitable for the apparatus employed (generally 0.2 to 1.0 g). The most suitable ignition improver shall be chosen from those given in 5. (13) of JIS Z 2615, and the improver of an amount most suitable for both the quantity of the sample and the combustion apparatus⁽⁶⁾ shall be either adequately mixed with the sample or placed all over the sample.

Note ⁽⁶⁾ In the case of a tubular electric-resistance furnace, for instance, mix the sample with 1.0 g of iron (powdery) containing as little carbon as possible and 1.5 g of tin (granular).

Alternatively, in the case of high-frequency induction furnace, mix the sample with 1.0 g of iron (powdery), and cover it with a mixture of 1.0 g of tungsten (granular) and 0.5 g of tin (granular).

5.3.6 Operation

5.3.6.1 Preparatory Operation Preparatory operation shall be carried out in accordance with the description in 6.6.4 (1) and (2) of JIS Z 2615.

In the case of using a tubular electric-resistance furnace, the temperature inside of the tube shall be maintained at 1300 to 1450°C⁽³⁾.

In the case of using a high-frequency induction furnace, the condition needed for running the high-frequency induction furnace should be established⁽⁴⁾.

5.3.6.2 Operation for Determination The operation for determination shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace
Follow the description in 6.6.5 of JIS Z 2615.
- (2) Case of Using High-Frequency Induction Furnace
 - (a) Place the crucible containing the sample and ignition improver on a rest, and close the tube for ignition. Circulate oxygen gas at a specified flow rate to replace air in the tube, and then run the high-frequency induction furnace.
 - (b) When the indicated value on a recorder or an indicator gradually rises and shows a constant value, read the indicated value, and take out the crucible after turning off the high-frequency switch.

5.3.7 Blank Test A blank test shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace Follow the description in 6.6.6 of JIS Z 2615.

- (2) Case of Using a High-Frequency Induction Furnace Use the crucible containing no sample but only the same quantity of ignition improver as that added to the sample, and carry out the procedures given in 5.3.6.2 (2).

In the case where use is made of the ignition improver that will generate no induced current by high-frequency current, 0.5 to 1.0 g of the iron or the like of a known and the lowest possible carbon content shall be used in this procedure, and the blank test value shall be decided on after making a correction of the amount of carbon contained in the added iron.

5.3.8 Preparation of Working Curve Select several kinds of standard specimens (3 or more pieces), which have a composition analogous to that of the sample and whose carbon contents comprehend the carbon contents of the sample, and carry out the operation in accordance with 5.3.6.2 on the specimens to acquire indicated values. After correction of these values making use of the value given by a blank test, prepare the working curve by plotting a relation curve showing the relation between the corrected values and the carbon contents (g) in the standard specimens.

When only one or two standard specimens, whose composition is similar to that of the sample, are available, choose a steel standard specimen with a suitable carbon content, and add this standard specimen to the similarly-composed standard specimen with the lowest possible carbon content either instead of iron to be added as an ignition improver or as a partial substitution of the improver. Then carry out the operation as described in 5.3.6.2. In this case, the total amount of carbon contained in the two specimens should be regarded as the carbon content.

In the absence of a standard specimen with a composition analogous to that of the sample, a steel standard specimen having an appropriate carbon content may serve. In this case, iron shall not be added as an ignition improver.

5.3.9 Calculation Determine the carbon quantity from the values obtained in 5.3.6.2 and 5.3.7 and from the working curve prepared in 5.3.8, and calculate the content of carbon in the sample from the following formula.

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

where, A_1 : quantity of carbon obtained from the measured value in 5.3.6.2 (g)

A_2 : quantity of carbon obtained from the measured value in 5.3.7 (g)

m : weighed out quantity of sample (g).

5.4 Combustion-Coulometric Method

5.4.1 Summary Completely oxidize carbon to change into carbon dioxide by heating the sample in an oxygen-gas flow, and allow the carbon dioxide to be absorbed in a weak alkaline barium salt solution having a specified pH value. Measure the quantity of electricity needed to restore pH decreased by the absorption to its original value through the electrolysis of a barium salt solution.

5.4.2 Reagents The reagents shall be as specified in 6.7.2 of JIS Z 2615.

5.4.3 Devices and Materials The devices and materials shall be as specified in 5. of JIS Z 2615.

5.4.4 Apparatus The apparatus shall be as specified in 6.7.3 of JIS Z 2615⁽⁵⁾.

5.4.5 Quantity of Sample and Ignition Improver The quantity of the sample to be weighed out shall be the one most suitable for the employed apparatus (generally 0.2 to 1.0 g). The most suitable ignition improver shall be selected from those given in 5. (13) of JIS Z 2615, and the improver of an amount most suitable for both the quantity of the sample and the combustion apparatus⁽⁶⁾ shall be either adequately mixed with the sample or placed all over the sample.

5.4.6 Operation

5.4.6.1 Preparatory Operation Preparatory operation shall be carried out in accordance with the description in 6.7.4 (1), (2) and (3) of JIS Z 2615.

In the case of using a tubular electric-resistance furnace, the temperature inside the tube shall be maintained at 1300 to 1450°C⁽³⁾.

In the case of using a high-frequency induction furnace, the condition needed for running the high-frequency induction furnace should be established⁽⁴⁾.

5.4.6.2 Operation for Determination The operation for determination shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace Follow the description in 6.7.5 of JIS Z 2615.
- (2) Case of Using High-Frequency Induction Furnace
 - (a) Place the crucible containing the sample and ignition improver on a rest, and close the tube for ignition. Circulate oxygen gas at a specified flow rate to replace air in the tube, then run the high-frequency induction furnace and simultaneously return the pointer to zero.

- (b) When the indicated value on an indicator gradually rises and shows a constant value, read the indicated value, and take out the crucible after turning off the high-frequency switch.

5.4.7 Blank Test A blank test shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace Follow the description in 6.7.6 of JIS Z 2615.
- (2) Case of Using High-Frequency Induction Furnace Use the crucible, containing no sample but only the same quantity of ignition improver as that added to the sample, and carry out the procedures given in 5.4.6.2 (2).

In the case where use is made of the ignition improver that will generate no induced current by high-frequency current, 0.5 to 1.0 g of the iron or the like of a known and the lowest possible carbon content shall be used in this procedure, and the blank test value shall be decided on after making a correction of the amount of carbon contained in the added iron.

5.4.8 Preparation of Working Curve Select several kinds of standard specimens (3 or more pieces), which have a composition analogous to that of the sample and whose carbon contents comprehend the carbon contents of the sample, and carry out the operation in accordance with 5.4.6.2 on the specimens to acquire indicated values. After correction of these values making use of the value given by a blank test, prepare the working curve by plotting a relation curve showing the relation between the corrected values and the carbon contents (g) in the standard specimens.

When only one or two standard specimens, whose composition is similar to that of the sample, are available, choose a steel standard specimen with a suitable carbon content, and add this standard specimen to the similarly-composed standard specimen with the lowest possible carbon content either instead of iron to be added as an ignition improver or as a partial substitution of the improver. Then carry out the operation as described in 5.4.6.2. In this case, the total amount of carbons contained in the two specimens should be regarded as the carbon content.

In the absence of a standard specimen with a composition analogous to that of the sample, a steel standard specimen having an appropriate carbon content may serve. In this case, iron shall not be added as an ignition improver.

5.4.9 Calculation Determine the carbon quantity from the values obtained in 5.4.6.2 and 5.4.7 and from the working curve prepared in 5.4.8, and calculate the content of carbon in the sample from the following formula.

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

where, A_1 : quantity of carbon obtained from the measured value in 5.4.6.2 (g)

A_2 : quantity of carbon obtained from the measured value in 5.4.7 (g)

m : weighed-out quantity of sample (g).

5.5 Combustion-Infrared Ray Absorption Method (Integration Method)

5.5.1 Summary Completely oxidize carbon to change into carbon dioxide by heating the sample in an oxygen-gas flow, and send this gas together with oxygen into an infrared-ray absorption cell to gauge the amount of the infrared ray absorbed by carbon dioxide.

5.5.2 Devices and Materials The devices and materials shall be as specified in 5. and 6.9.2 of JIS Z 2615.

5.5.3 Apparatus The apparatus shall be as specified in 6.9.3 of JIS Z 2615⁽⁷⁾.

Note ⁽⁷⁾: A tubular electric-resistance furnace may be used.

5.5.4 Quantity of Sample and Ignition Improver The quantity of the sample to be weighed out shall be the one most suitable for the employed apparatus (generally 0.2 to 1.0 g). The most suitable ignition improver shall be selected from those given in 5. (13) of JIS Z 2615, and the improver of an amount most suitable for both the quantity of the sample and the combustion apparatus⁽⁶⁾ shall be either adequately mixed with the sample or placed all over the sample.

5.5.5 Operation

5.5.5.1 Preparatory Operation Preparatory operation shall be carried out in accordance with the description in 6.9.4 (1) and (2) of JIS Z 2615.

In the case of using a tubular electric-resistance furnace, the temperature inside the tube shall be maintained at 1300 to 1450°C⁽³⁾.

In the case of using a high-frequency induction furnace, the condition needed for running the high-frequency induction furnace shall be established⁽⁴⁾.

5.5.5.2 Operation for Determination The operation for determination shall be carried out in accordance with either of the following.

(1) Case of Using Tubular Electric-Resistance Furnace

- (a) Insert the boat loaded with weighed-out sample and ignition improver into the center of the ignition tube, and send oxygen gas at a specified flow rate into the apparatus employed.

- (b) Read the indicated value when the pointer of the indicator gives a constant value after a gradual increment.
- (2) Case of Using High-Frequency Induction Furnace Follow the description in 6.9.5 of JIS Z 2615.

5.5.6 Blank Test A blank test shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace Use the boat containing no sample but only the same quantity of an ignition improver as that added to the sample in the furnace, and carry out the procedures given in 5.5.5.2 (1).
- (2) Case of Using High-Frequency Induction Furnace Follow the description in 6.9.6 of JIS Z 2615.

5.5.7 Preparation of Working Curve Select several kinds of standard specimens (3 or more pieces), which have a composition analogous to that of the sample and whose carbon contents comprehend the carbon contents of the sample, and carry out the operation in accordance with 5.5.5.2 on the specimens to acquire indicated values. After correction of these values making use of the value given by a blank test, prepare the working curve by plotting a relation curve showing the relation between the corrected values and the carbon contents (g) in the standard specimens.

When only one or two standard specimens, whose composition is similar to that of the sample, are available, choose a steel standard specimen with a suitable carbon content, and add this standard specimen to the similarly-composed standard specimen with the lowest possible carbon content either instead of iron to be added as an ignition improver or as a partial substitution of the improver. Then carry out the operation as described in 5.5.5.2. In this case, the total amount of carbons contained in the two specimens should be regarded as the carbon content.

In the absence of a standard specimen with a composition analogous to that of the sample a steel standard specimen having an appropriate carbon content may serve. In this case, iron shall not be added as an ignition improver.

5.5.8 Calculation Determine the carbon quantity from the values obtained in 5.5.5.2 and 5.5.6 and from the working curve prepared in 5.5.7, and calculate the content of carbon in the sample from the following formula.

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

where, A_1 : quantity of carbon obtained from the measured value in 5.5.5.2 (g)

A_2 : quantity of carbon obtained from the measured value in 5.5.6 (g)

m : weighed-out quantity of sample (g).

5.6 Combustion-Infrared Ray Absorption Method (Circulation Method)

5.6.1 Summary Heat the sample in a circulating oxygen gas flow which has a specified volume under a definite pressure to oxidize carbon into carbon dioxide and carbon monoxide, and send these gases together with superfluous oxygen into an absorption infrared ray detector set in the circulation loop. Measure the infrared rays absorbed by carbon dioxide and carbon monoxide respectively.

5.6.2 Devices and Materials The devices and materials shall be as specified in 5. and 6.9.2 of JIS Z 2615.

5.6.3 Apparatus The apparatus shall be as specified in 6.10.2 of JIS Z 2615⁽⁷⁾.

5.6.4 Quantity of Sample and Ignition Improver The quantity of the sample shall be the one most suitable for the apparatus employed (generally 0.2 to 1.0 g). The most suitable ignition improver shall be selected from those given in 5. (13) of JIS Z 2615, and the improver, of an amount most suitable for both the quantity of the sample and the combustion apparatus⁽⁶⁾ shall be either adequately mixed with the sample or placed all over the sample.

5.6.5 Operation

5.6.5.1 Preparatory Operation Preparatory operation shall be carried out in accordance with the description in 6.10.3 (1) and (2) of JIS Z 2615.

In the case of using a tubular electric-resistance furnace, the temperature inside the tube shall be maintained at 1300 to 1450°C⁽³⁾.

In the case of using a high-frequency induction furnace, the condition needed for running the high-frequency induction furnace shall be established⁽⁴⁾.

5.6.5.2 Operation of Determination The operation for determination shall be carried out in accordance with either of the following.

(1) Case of Using Tubular Electric-Resistance Furnace

- (a) Insert the boat loaded with weighed-out sample and ignition improver in the center of an ignition tube, and send oxygen gas at a specified flow rate into the apparatus employed.
- (b) Read the indicated value when the indicator has given a constant value after a gradual increment.

(2) Case of Using High-Frequency Induction Furnace Follow the description in 6.10.4 of JIS Z 2615.

5.6.6 Blank Test A blank test shall be carried out in accordance with either of the following.

- (1) Case of Using Tubular Electric-Resistance Furnace Use the boat containing no sample but only the same quantity of an ignition improver as that added to the sample in the furnace, and carry out the procedures given in 5.6.5.2 (1).
- (2) Case of Using High-Frequency Induction Furnace Follow the description in 6.10.5 of JIS Z 2615.

5.6.7 Preparation of Working Curve Select several kinds of standard specimens (3 or more pieces), which have a composition analogous to that of the sample and whose carbon contents comprehend the carbon contents of the sample, and carry out the operation in accordance with 5.6.5.2 on the specimens to acquire indicated values. After correction of these values making use of the value given by a blank test, prepare the working curve by plotting a relation curve showing the relation between the corrected values and the carbon contents (g) in the standard specimens.

When only one or two standard specimens, whose composition is similar to that of the sample, are available, choose a steel standard specimen with a suitable carbon content, and add this standard specimen to the similarly-composed standard specimen with the lowest possible carbon content either instead of iron to be added as an ignition improver or as a partial substitution of the improver. Then carry out the operation as described in 5.6.5.2. In this case, total amount of carbons contained in the two specimens should be regarded as the carbon content.

In the absence of a standard specimen with a composition analogous to that of the sample, a steel standard specimen having an appropriate carbon content may serve. In this case, iron shall not be added as an ignition improver.

5.6.8 Calculation Determine the carbon quantity from the values obtained in 5.6.5.2 and 5.6.6 and from the working curve prepared in 5.6.7, and calculate the content of carbon in the sample from the following formula.

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

where A_1 : quantity of carbon obtained from the measured value in 5.6.5.2 (g)

A_2 : quantity of carbon obtained from the measured value in 5.6.6 (g)

m : weighed-out quantity of sample (g).

6. Method for Determination of Phosphorus

6.1 Determination Method The determination of phosphorus shall be in accordance with a molybdenum-blue absorptiometry. This method can be used for the sample containing less than 0.08 wt % of phosphorus.

6.2 Absorptiometry by Molybdenum Blue

6.2.1 Summary Decompose the sample using nitric acid and hydrofluoric acid, let it generate white fume by adding perchloric acid to oxidize to orthophosphoric acid, reduce iron and the like by adding sodium hydrogen sulfite, add coloring agents containing hexaammonium heptamolybdate and hydrazinium sulfate (2+), and heat to produce molybdenum blue. Measure its absorbance.

6.2.2 Reagents The reagents shall be as follows.

- (1) Nitric acid
- (2) Perchloric acid (60 wt %)
- (3) Hydrofluoric acid
- (4) Sodium hydrogensulfite solution (100 g/l)
- (5) Coloring agent solution At time of use mix 25 ml of solution A, 10 ml of solution B and 65 ml of water, which follow.

Solution A: Dissolve 20 g of hexaammonium heptamolybdate tetrahydrate in 300 ml of water, add 650 ml of sulfuric acid (1+1) and, after cooling, dilute with water up to 1 l .

Solution B: Hydrazinium sulfate (2+) solution (1.5 g/l)

- (6) Standard phosphorus solution (100 ug P/ml) Weigh out 0.4394 g of potassium dihydrogen phosphate (KH_2PO_4) which has been dried at 110°C and cooled in a desiccator to room temperature to a constant mass, and dissolve it in water. Transfer this solution into a 1000-ml volumetric flask while rinsing the beaker with water, and dilute it with water up to the marked line.

6.2.3 Quantity of Sample Weigh out 1.0 g of sample.

6.2.4 Operation

6.2.4.1 Preparation of Sample Solution The preparation of sample solution shall be carried out as follows.

- (1) Weigh out the sample in either a platinum dish (No. 100) or a beaker (200 ml) made of polyethylene tetrafluoride, and decompose it by adding 20 ml of nitric acid and dripping about 5 ml of hydrofluoric acid. If the reaction becomes

too violent, cool it down with water during decomposition. Heat to evaporate the solution by adding 10 ml of perchloric acid, and let the white fume of perchloric acid emit for about 5 min in order to dispel hydrofluoric acid. After cooling, transfer the solution to a beaker (200 ml) while rinsing with warm water. Cover it with a watch glass, heat until it emits white fume again. Continue to heat it further for about 10 min under the condition that the inside of the beaker becomes transparent and the vapor of perchloric acid is refluxed along the inside walls of the beaker. After cooling, add about 30 ml of warm water to dissolve soluble salts. Remove the watch glass while rinsing its reverse side with water, add the washings to sample solution, filtrate the solution through a filter paper (Grade 5 A) into a 100-ml volumetric flask, and wash the filter paper with warm water several times.

- (2) Cool the solution to room temperature, and then dilute it up to the marked line.

6.2.4.2 Coloring Accurately pipette an aliquot of 10 ml from the solution obtained in 6.2.4.1 into a 100-ml volumetric flask, add 10 ml of sodium hydrogensulfite, agitate and heat the solution until the color of the solution turns colorless in a boiling water bath. Next, add 25 ml of the coloring agent (6.2.2 (5)), agitate and heat for 20 min in a boiling water bath. After cooling to room temperature in running water, dilute it with water up to the marked line.

6.2.4.3 Measurement of Absorbance Transfer a portion of the solution obtained in 6.2.4.2 to an absorption cell (10 mm, made of glass), and measure its absorbance in the vicinity of the wavelength of 825 nm using water as a contrast solution.

6.2.5 Blank Test Carry out the blank test using only the reagents concurrently with the sample test in accordance with the procedures described in 6.2.4.1 to 6.2.4.3.

6.2.6 Preparation of Working Curve Pipette graded quantities of several aliquots from 0 ml to 8.0 ml (0 to 800 μg as phosphorus) of the standard phosphorus solution [6.2.2 (6)], into as many beakers (200 ml each), and cover each with watch glass. Add 5 ml each of perchloric acid, and heat it to emit white fume. Continue to heat it further for about 10 min under the condition that the inside of the beaker becomes transparent and the vapor of perchloric acid is refluxed along the inside walls of the beaker. After cooling, remove the watch glass while rinsing it with water, add about 50 ml of warm water and transfer the solution to a 100-ml volumetric flask while rinsing the beaker with water. Hereafter treat it in accordance with the procedures described in 6.2.4.1 (2) to 6.2.4.3. Plot the curve indicating the relation between the absorbances measured and the quantities of phosphorus, and parallel shift the curve in such a way that it passes the origin. Thus the working curve is completed.

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6.2.7 Calculation Obtain the quantity of phosphorus from both the remainder of absorbance after the subtraction of the one in 6.2.5 from the one in 6.2.4.3, and the working curve prepared in 6.2.6. Calculate the phosphorus content in the sample from the following formula.

$$\text{Phosphorus wt \%} = \frac{A}{m \times B} \times 100$$

where, A : quantity of phosphorus detected in pipetted sample solution (g)

m : weighed-out quantity of the sample (g)

B : aliquot ratio of sample solution and blank solution.

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