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JAPANESE INDUSTRIAL STANDARD

Methods for Chemical Analysis of Ferrosilicon

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Methods for Chemical Analysis of Ferrosilicon

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1. Scope

This Japanese Industrial Standard specifies the methods for determination of silicon, carbon, phosphorus, sulphur, and aluminium in ferrosilicon.

Remark: The units and numerical values given in { } in this Standard are based on the traditional units and are appended for informative reference.

2. General Matters

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

3. Methods for Determination of Silicon

3.1 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 applies to the whole range of silicon content in ferrosilicon.
- (2) Potassium Hexafluorosilicate Precipitation Separation Sodium Hydroxide Titrimetric Method This method applies to the whole range of silicon content in ferrosilicon.

3.2 Silicon Dioxide Gravimetric Method

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

JIS Z 2616-General Rules for Determination of Sulfur in Metallic Materials

Corresponding International Standards:

ISO 4139 Ferrosilicon-Determination of aluminium content-Flame atomic absorption spectrometric method

ISO 4158 Ferrosilicon, ferrosilicomanganese and ferrosilicochromium-Determination of silicon content-Gravimetric method

3.2.1 Summary Fuse a sample with fusing mixture or sodium hydroxide, add hydrochloric acid and perchloric acid, evaporate by heating, and make silicon into insoluble silicic acid. Ignite the precipitate. After measuring the mass, treat with hydrofluoric acid, vaporize silicon dioxide, and measure the mass.

3.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1+1, 1+2, 1+10)
- (2) Perchloric acid (60 wt%)
- (3) Hydrofluoric acid
- (4) Sulphuric acid (1+1, 1+3)
- (5) Sodium hydroxide
- (6) Fusing mixture [sodium peroxide 2 parts, sodium carbonate (anhydride) 1 part]
- (7) Sodium thiocyanate solution (100 g/l)

3.2.3 Weighing Out Amount of Sample The weighing out amount of a sample shall be 0.20 g.

3.2.4 Operation

3.2.4.1 Decomposition of Sample The decomposition of a sample shall be in accordance with either of the following methods:

- (1) **For Fusion by Using Fusing Mixture** Weigh out a sample, transfer to a nickel crucible (30 ml) or a zirconium crucible (30 ml), add 5 g of fusing mixture, sufficiently mix by stirring, cover them with 1 g of fusing mixture, cover, and heat initially at low temperature, and heat until the contents are melted down while the crucible is being rotated. Then, raise temperature, heat the crucible at about 700°C (dark red heat) for about 5 min while the crucible is being shaken, and thoroughly fuse. Thereafter, allow to stand to cool. Put the crucible together with the cover into a beaker (500 ml) containing 60 ml of hydrochloric acid (1+2). After dissolving the melt, wash the crucible and cover with water, and take out.
- (2) **For Fusion by Using Sodium Hydroxide** Weigh out a sample, transfer to a nickel crucible (30 ml) or a zirconium crucible (30 ml), add 5 g of sodium hydroxide, sufficiently mix by stirring, and thoroughly dehydrate on a hot plate. Thereafter, cover it, and carefully fuse by gradually increasing temperature. After standing to cool, put the crucible and cover into a polyethylene beaker (300 ml) containing about 100 ml of warm water, dissolve the melt, wash the crucible and cover with water, and take out. After cooling this solution to room temperature, and transfer to a beaker (500 ml) containing 20 ml of hydrochloric acid by washing with water.

3.2.4.2 Dehydration Treatment of Silicic Acid Add 40 ml of perchloric acid to the solution obtained in 3.2.4.1, evaporate by heating on a sand bath, and generate thick white fume. Thereafter, cover it with a watch glass. Continue to heat for about 15 min under a state wherein the vapour of perchloric acid is refluxed along the inner wall of a beaker. After standing to cool, add 20 ml of hydrochloric acid (1+1) and about 100 ml of warm water, and dissolve the soluble salts. Wash the watch glass with water, remove it, and immediately filter by using filter paper (class 5 A). Receive the filtrate with other beaker (500 ml). Rub the precipitate stuck to the inner wall of the beaker and the watch glass off with a policeman (glass rod with rubber), and transfer onto the filter paper by washing with warm hydrochloric acid (1+10). Thereafter, wash initially five times with warm hydrochloric acid (1+10) and then with warm water until reaction of iron ion disappears in the filtrate⁽¹⁾. Reserve the precipitate together with the filter paper as a main precipitate.

Note (1) Take a portion of the washings, add potassium thiocyanate solution, and wash until the coloration of orange red is not presented.

3.2.4.3 Recovery of Silicon Dioxide Add 10 ml of perchloric acid to the filtrate and washings obtained in 3.2.4.2, and evaporate by heating on a sand bath. After generating thick white fume, cover it with a watch glass. Continue to heat for about 15 min under a state in which the vapour of perchloric acid is refluxed along the inner wall of a beaker. After standing to cool, add 20 ml of hydrochloric acid (1+1) and about 100 ml of warm water, and dissolve the soluble salts. Wash the watch glass with water to be removed, and immediately filter by using filter paper (class 5 B). Rub the precipitate stuck to the inner wall of the beaker and the watch glass off with a policeman, and transfer onto the filter paper by washing with warm hydrochloric acid (1+10). Thereafter, wash initially five times with warm hydrochloric acid (1+10) and then with warm water until reaction of iron ion disappears⁽¹⁾ in the filtrate. Discard the filtrate and washings.

3.2.4.4 Incineration and Weighing Carry out the incineration and weighing in accordance with the following procedures:

- (1) Transfer the precipitate obtained two times in 3.2.4.2 and 3.2.4.3 together with the filter paper to a platinum crucible (No. 30). After drying, incinerate the filter paper by gradually heating.
- (2) After ignition at about 1100°C for about 30 min, allow to stand to cool in a desiccator to room temperature, and measure the mass. Repeat this operation to constant weight.

3.2.4.5 Hydrofluoric Acid Treatment and Weighing Carry out the hydrofluoric acid treatment and weighing in accordance with the following procedures:

- (1) Moisten the precipitate in a platinum crucible obtained in 3.2.4.4 by adding 2 to 3 drops of sulphuric acid (1+3) thereto, add 3 to 5 ml hydrofluoric acid, and vaporize silicon dioxide and sulphuric acid by carefully heating.

- (2) After ignition at about 1100°C for about 30 min, allow to stand to cool to room temperature in a desiccator, and measure the mass. Repeat this operation to constant weight.

3.2.5 Blank Test Use only reagents, and operate concurrently with a sample following the procedures of 3.2.4.1 to 3.2.4.5.

3.2.6 Calculation Calculate the content of silicon in a 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 in 3.2.4.4 (2) of the sample (g)
 - m_2 : mass obtained in 3.2.4.5 (2) of the sample (g)
 - m_3 : mass obtained in 3.2.4.4 (2) in blank test (g)
 - m_4 : mass obtained in 3.2.4.5 (2) in blank test (g)
 - m_0 : weighing out amount of sample (g)

3.3 Potassium Hexafluorosilicate Precipitation Separation Sodium Hydroxide Titrimetric Method

3.3.1 Summary Decompose a sample with hydrofluoric acid containing nitric acid and potassium fluoride, and precipitate potassium hexafluorosilicate. After fusing a sample difficult to be dissolved in acid with fusing mixture, sodium hydroxide, or potassium hydroxide, dissolve in nitric acid, and add hydrofluoric acid and potassium nitrate to precipitate potassium hexafluorosilicate. Filter the precipitate, dissolve in warm water, and titrate with sodium hydroxide standard solution.

3.3.2 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 part and potassium carbonate (anhydride) 5 parts]
- (7) Potassium nitrate
- (8) Potassium nitrate solution (50 g/l) Since sodium nitrate solution is occasionally alkalified, it has been preliminarily neutralized with nitric acid in that case.
- (9) Potassium fluoride solution Dissolve 200 g of potassium fluoride in hydrofluoric acid to 1 l.
- (10) 0.5 mol/l sodium hydroxide standard solution (20.0 g NaOH/l) The preparation and standardization method thereof shall be in accordance with 4.4 (20.2) of JIS K 8001.

- (11) Phenolphthalein solution Dissolve 0.5 g of phenolphthalein in 100 ml of ethanol (95).

3.3.3 Weighing out Amount of Sample The weighing out amount of a sample shall be, as a rule, as given in Table 1.

Table 1. Weighing out Amount of Sample

Content of silicon wt%	Weighing out amount of sample g
Under 40	0.20
40 min.	0.10

3.3.4 Operation

3.3.4.1 Decomposition of Sample and Generation of Precipitate

The decomposition of sample and generation of precipitates shall be in accordance with either one of the following:

- (1) Sample Easy to Be Decomposed with Acid Weigh out a sample, transfer to a polyethylene beaker (300 ml), add 30 ml of nitric acid (1+1), cover it with a polyethylene or platinum cover, and decompose by adding little by little 10 ml of potassium fluoride solution [3.3.2 (9)] while it is being mixed by shaking. Then, increase the amount of solution to about 80 ml by adding 5 ml of hydrochloric acid and water. After heating on a water bath for about 15 min, add a small amount of filter paper pulp, allow to stand still for about 30 min while it is being cooled to 15°C or lower, and generate the precipitate of potassium hexafluorosilicate.
- (2) Sample Difficult to Be Decomposed with Acid
 - (2.1) For Fusion by Using Fusing Mixture Weigh out a sample, transfer to a nickel crucible (30 ml) or a zirconium crucible (30 ml), add 3 g of fusing mixture, and sufficiently mix by stirring. Cover it, and initially heat at a low temperature until the contents are melted down while the crucible is being rotated. Then, increase temperature, and heat the crucible at about 700°C (dark red heat) for about 5 min while it is being shaken to be thoroughly fused. After standing to cool, add a small amount of warm water to the crucible, and dissolve the melt by gently heating. Transfer the solution to a polyethylene beaker (300 ml) containing 50 ml of nitric acid (1+1) by washing. Add 3 ml of hydrochloric acid to the crucible, dissolve the melt stuck to the inner wall, and further wash the crucible together with the cover with water. Heat it on a water bath, and dissolve thoroughly the melt. After dilution to about 80 ml by adding water, add 10 ml of hydrofluoric acid and 3 g of potassium nitrate, mix by stirring, and heat on a water bath for about 15 min. Add a small amount of filter paper pulp, allow to stand still for about 30 min while it is being cooled to 15°C or lower, and generate the precipitate of potassium hexafluorosilicate.

- (2.2) For Fusion by Using Alkali Hydroxide Weigh out a sample, transfer to a nickel crucible (30 ml) or a zirconium crucible (30 ml), add 3 g of sodium hydroxide or potassium hydroxide, and sufficiently mix by stirring. After thorough dehydration on a hot plate, cover it, and carefully fuse by gradually increasing temperature. After standing to cool, add a small amount of warm water to the crucible, and dissolve the melt by gently heating. Transfer the solution to a polyethylene beaker (300 ml) containing 50 ml of nitric acid (1+1) by washing. Add 3 ml of hydrochloric acid to the crucible to dissolve the melt stuck to the inner wall and further, sufficiently wash the crucible together with the cover again with water. Heat it on a water bath, and thoroughly dissolve the melt. After dilution to about 80 ml by adding water, add 10 ml of hydrofluoric acid and 3 g of potassium nitrate, mix by stirring, and heat on a water bath for about 15 min. Add a small amount of filter paper pulp, allow to stand still for about 30 min while it is being cooled to 15°C or lower, and generate the precipitate of potassium hexafluorosilicate.

3.3.4.2 Filtration and Washing Filter the precipitate of hexafluoro-silicate obtained in 3.3.4.1 with a polyethylene funnel by using filter paper (class 5 A) while it is being cooled at 15°C or lower. Then, wash generally 15 times by potassium nitrate solution [3.3.2 (8)] cooled at 15°C or lower until blue litmus paper does not turn red. Transfer the precipitate together with the filter paper to an Erlenmeyer flask (200 ml), add about 50 ml of warm water, sufficiently mix by shaking, and crush the filter paper.

3.3.4.3 Titration After boiling the solution obtained in 3.3.4.2, immediately add several drops of phenolphthalein solution [3.3.2 (11)] as the indicator, and add 0.5 mol/l sodium hydroxide standard solution [3.3.2 (10)] to near the end point at one time. Further, after adding several drops of phenolphthalein solution [3.3.2 (11)], titrate again with 0.5 mol/l sodium hydroxide standard solution [3.3.2 (10)], and take the point at which the solution turns faint red as the end point.

3.3.5 Blank Test Use only reagents, and operate concurrently with a sample following the procedures of 3.3.4.1 to 3.3.4.3.

3.3.6 Calculation Calculate the content of silicon in a sample from the following formula:

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

- where
- V_1 : used amount of 0.5 mol/l sodium hydroxide standard solution obtained in 3.3.4.3 (ml)
 - V_2 : used amount of 0.5 mol/l sodium hydroxide standard solution obtained in 3.3.5 (ml)
 - F : factor of 0.5 mol/l sodium hydroxide standard solution
 - m : weighing out amount of sample (g)

4. Methods for Determination of Carbon

4.1 Classification of Determination Methods The method for determination of carbon shall be in accordance with either one of the following methods:

- (1) Combustion - Gas Volumetric Method This method applies to the sample of 0.05 wt% or over in carbon content.
- (2) Combustion - Conductometric Method This method applies to the sample of 0.005 wt% or over in carbon content when a tubular electric resistance heating furnace is used as a combustion equipment and the sample of 0.01 wt% or over in carbon content when a high frequency induction heating furnace is used.
- (3) Combustion - Coulometric Method This method applies to the sample of 0.005 wt% or over in carbon content when a tubular electric resistance heating furnace is used as the combustion equipment and the sample of 0.01 wt% or over in carbon content when a high frequency induction heating furnace is used.
- (4) Combustion - Infrared Absorption Method This method applies to the sample of 0.005 wt% or over in carbon content when a tubular electric resistance heating furnace is used as the combustion equipment and to the sample of 0.01 wt% or over in carbon content when a high frequency induction heating furnace is used.

4.2 Combustion - Gas Volumetric Method

4.2.1 Summary Heat a sample in an oxygen gas current, sufficiently oxidize carbon to carbon dioxide, collect it together with oxygen into a buret, measure the volume of gas, then absorb carbon dioxide in alkali to be removed, and measure the volume of remaining gas.

4.2.2 Appliances and Materials The appliances and materials shall be in accordance with 5. of JIS Z 2615.

4.2.3 Apparatus The apparatus shall be in accordance with 6.3.2 of JIS Z 2615.

4.2.4 Weighing out Amount of Sample and Additional Amount of Ignition Improver Allow the weighing out amount of a sample to be, as a rule, as given in Table 2. For ignition improver, select the most optimum one among those given in 5. (13) of JIS Z 2615, add the weighing out amount of the sample and the amount most optimum for a combustion equipment, and sufficiently mix, or otherwise cover the sample thereby.

Table 2. Weighing out Amount of Sample

Carbon content wt%	Weighing out amount of sample g
0.05 up to and excluding 0.3	2.0
0.3 up to and excluding 1.0	1.0
1.0 min.	0.50

4.2.5 Operation

4.2.5.1 Preparatory Operation The preparatory operation shall be in accordance with 6.3.3 of JIS Z 2615.

Further, when a tubular electric resistance heating furnace is used, a temperature in the combustion tube shall be kept at 1300 to 1450°C⁽²⁾.

Furthermore, when a high frequency induction heating furnace is used, conditions⁽³⁾ related to the high frequency induction heating furnace shall be established.

Notes ⁽²⁾ When there is any difference between the temperature indication of a pyrometer and a temperature in the combustion tube, correction is performed.

⁽³⁾ The conditions herein mean conditions determined according to the specifications of an apparatus to be used, such as the anode current, grid current, etc. of a high frequency oscillator.

4.2.5.2 Determinating Operation The determinating operation shall be carried out in accordance with either one of the following cases:

- (1) When Tubular Electric Resistance Heating Furnace Is Used
The determinating operation shall be carried out as described 6.3.4 of JIS Z 2615.
- (2) When High Frequency Induction Heating Furnace Is Used
The determinating operation shall be carried out as described in 6.3 Remark of JIS Z 2615.

4.2.6 Blank Test The blank test shall be carried out in accordance with either one of the following cases:

- (1) When Tubular Electric Resistance Heating Furnace Is Used
The blank test shall be carried out as described in 6.3.5 of JIS Z 2615.
- (2) When High Frequency Induction Heating Furnace Is Used Use a crucible containing only the same ignition improver as those added to a sample without containing the sample, and perform the operation of 4.2.5.2 (2).

Further, when the ignition improver in which a induction current is not generated by a high frequency current is used, perform the operation by adding 0.5 to 1.0 g of the iron or the like of which the carbon content is as low as possible and known, correct by the amount of carbon contained in the added iron or the like, and adopt the result as a blank test value.

4.2.7 Calculation The calculation shall be carried out in accordance with 6.3.6 of JIS Z 2615.

4.3 Combustion - Conductometric Method

4.3.1 Summary Heat a sample in an oxygen gas current, sufficiently oxidize carbon to carbon dioxide, absorb in a definite amount of alkali solution, and measure variation of the conductivity of the alkali solution before and after absorption.

4.3.2 Reagents The reagents shall be as described in 6.6.2 of JIS Z 2615.

4.3.3 Appliances and Materials The appliances and materials shall be as described in 5. of JIS Z 2615. However, ignition improvers shall be as follows:

- (1) Iron (III) Oxide Reagent powdery iron (III) oxide which has been preliminarily burnt at 900°C for 2 h and is let to stand to cool in a desiccator.
- (2) Lead Lead of a rod or plate form, of which a blank test value is as low as possible, is cut just before service and is used.
- (3) Iron Pure iron, of which a blank test value is as low as possible.
- (4) Tin Powdery tin, of which a blank test value is as low as possible.
- (5) Tungsten Granular tungsten, of which a blank test value is as low as possible.

4.3.4 Apparatus The apparatus shall be as described in 6.6.3 of JIS Z 2615⁽⁴⁾.

Note (4) A high frequency induction heating furnace may be used instead of a tubular electric resistance heating furnace. When the high frequency induction heating furnace is used, for instance, reads of a boat and a boat cover are replaced by reads of a crucible and a cover.

4.3.5 Weighing out Amount of Sample The weighing out amount of a sample shall be 0.50 g.

4.3.6 Operation

4.3.6.1 Preparatory Operation The preparatory operation shall be as described in 6.6.4 (1) and (2) of JIS Z 2615.

Further, when a tubular electric resistance heating furnace is used, a temperature in the combustion tube shall be kept at 1350°C⁽²⁾.

Furthermore, when a high frequency induction heating furnace is used, conditions⁽³⁾ relating to the high frequency induction heating furnace shall be established.

4.3.6.2 Determining Operation The determining operation shall be carried out in accordance with either one of the following cases. However, the classification, additional amount, and additional method of ignition improvers shall be as given in Table 3.