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JAPANESE INDUSTRIAL STANDARD

Methods for Chemical Analysis of Silicomanganese

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Methods for Chemical Analysis of
Silicomanganese

G 1314-1987

1. Scope

This Japanese Industrial Standard specifies methods for determination of manganese, silicon, carbon, phosphorus and sulphur in silicomanganese.

2. General Items

The general items common to methods for chemical analysis shall be in accordance with JIS G 1301.

3. Methods for Determination of Manganese

3.1 Division of Methods for Determination The method for determination of manganese shall be in accordance with either one of the following:

- (1) Potassium Permanganate Direct Titration Method This method applies to the whole range of silicomanganese.
- (2) EDTA Titration Method This method applies to the whole range of silicomanganese.
- (3) Potentiometric Titration Method This method applies to the whole range of silicomanganese.

3.2 Potassium Permanganate Direct Titration Method

Applicable Standards:

JIS G 1301-General Rules for Chemical Analysis of Ferro-alloys

JIS K 0113-General Rules for Methods of Potentiometric, Amperometric, and Coulometric Titrations

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 4159 Ferromanganese and ferrosilicomanganese-Determination of manganese content-Potentiometric method

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

3.2.1 Summary The sample is decomposed by nitric acid and hydrofluoric acid, white-fume treated by adding sulfuric acid to remove nitric acid. It is neutralized with zinc oxide to separate iron and the like, and titrated by potassium permanganate standard solution.

3.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1)
- (2) Nitric acid
- (3) Hydrofluoric acid (46 %)
- (4) Sulfuric acid (1 + 1)
- (5) Sodium disulfate
- (6) Zinc oxide milk Add water to zinc oxide to make milky state.
- (7) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4 /l) The preparation, standardization and preservation methods shall be in accordance with 4.4 (9) of JIS K 8001.

3.2.3 Weighing-Out Amount of Sample The weighing-out amount of sample shall be 0.10 g and weighed out to the nearest 0.1 mg.

3.2.4 Operation The determination operation shall be carried out according to the following procedures:

- (1) **Preparation of Sample Solution** Transfer the weighed-out sample into a platinum pan (No. 100) or a beaker (100 ml) made of polytetrafluoroethylene, add nitric acid of 15 ml, and drop to add each several drops of hydrofluoric acid to decompose. In this case, when the reaction has become violent, decompose it by cooling with water. Add to this sulfuric acid (1 + 1) 10 ml to evaporate by heating, and generate vigorously white fume of sulfuric acid for about 10 min. After standing to cool ⁽¹⁾, add water about 30 ml, and after dissolving the soluble salts by heating transfer with washing into a beaker (300 ml) ⁽²⁾.

Notes ⁽¹⁾ At this time, in the case of existing of colored insoluble contents, add hydrochloric acid (1 + 1) about 5 ml to heat and again let generate white fume of sulfuric acid.

- ⁽²⁾ In the case of existing of undecomposed residue, filter the sample solution by using filter paper (Class 5 A) and wash with warm water several times. Receive the filtrate and washings into a beaker (300 ml) and preserve as the main solution. Put the residue together with the filter paper into a platinum crucible (No. 30) to incinerate. After standing to cool, add sodium disulfate about 2 g and heat to fuse. After standing to cool, put in the main solution preserved preliminarily together with the platinum crucible, and heat to dissolve the melt. Take out the platinum crucible by washing with a small amount of water.

- (2) Removing Iron and the Like After making the sample solution obtained in (1) about 100 ml with water, add little by little zinc oxide milk to neutralize, further add its small excess and heat until it boils. Filter the precipitates together with the excess zinc oxide by using filter paper (Class 5 A) and wash sufficiently with warm water. Allow the filtrate and washings to be white turbid. Receive the filtrate and washings in an Erlenmeyer flask (500 ml), and add hot water to dilute to about 200 ml. Add to this 1 or 2 drops of zinc oxide milk to be white turbid. Discard the precipitates.
- (3) Titration After heating the sample solution obtained in (2) to boil, immediately titrate it by potassium permanganate standard solution of 0.02 mol/l, and take the point where the faint pink color of supernatant liquid does not disappear even though it is boiled for about 1 min since the solution has colored to faint pink as the end point.

3.2.5 Calculation The content of manganese in the sample shall be calculated according to the following formula:

$$\text{Manganese (\%)} = \frac{V \times 0.001648}{W} \times 100$$

where V : used amount of potassium permanganate standard solution of 0.02 mol/l (ml)

W : weighed out amount of sample (g)

3.2.6 Analysis Precision The analysis precision according to this method shall be in accordance with Table 1.

Table 1

Manganese content % (3)	Standard deviation in a laboratory	Standard deviation between laboratories
62.49	0.096	0.114

Note (3) This value is the manganese content of sample used for deciding the analysis precision.

3.3 EDTA Titration Method

3.3.1 Summary After decomposing the sample with nitric acid and hydrofluoric acid, it is made acidic with hydrochloric acid, and thereafter hydroxyl ammonium chloride and triethanolamine is added. pH is adjusted at about 10, potassium cyanide is added and it is titrated by EDTA standard solution with using Thymolphthalein complexon as indicator.

3.3.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1)

- (2) Nitric acid
- (3) Hydrofluoric acid (46 %)
- (4) Potassium cyanide solution (10 g/l)
- (5) Sodium disulfate
- (6) Ammonium buffer solution After dissolving ammonium chloride 54 g in water, add aqueous ammonia 600 ml, and make 1000 ml with water.
- (7) Hydroxyl ammonium chloride solution (50 g/l)
- (8) Triethanolamine solution (1 + 4)
- (9) 0.05 mol/l ethylenediaminedisodium tetraacetate, hereinafter referred to as the EDTA, standard solution (18.613 g $C_{10}H_{14}O_8 N_2Na_2 \cdot 2 H_2O/l$)
The preparation, standardization and preservation methods shall be in accordance with 4.4 (5) (5.2) of JIS K 8001.
- (10) Thymolphthalein complexon (TPC) indicator Add potassium nitrate 10 g to Thymolphthalein complexon ($C_{38}H_{44}N_2O_{12}$) of 0.1 g and mix thoroughly by rubbing with agate mortar.

3.3.3 Weighing-Out Amount of Sample The weighing-out amount of sample shall be 0.10 g and, weighed out to the nearest 0.1 mg.

3.3.4 Operation The determination operation shall be carried out according to the following procedures:

- (1) Preparation of Sample Solution Transfer the weighed-out sample into a platinum pan (No. 100) or a beaker (100 ml) made of polytetrafluoroethylene, add nitric acid 15 ml, and add by dropping each several drops of hydrofluoric acid to decompose. At this time where the reaction has become vigorous, decompose while cooling with water. Next, heat to evaporate to dryness, and further heat strongly. After standing to cool, add hydrochloric acid (1 + 1) 10 ml and heat to dissolve soluble salts ⁽²⁾.
- (2) Titration Transfer the sample solution obtained in 3.3.4 (1) into an Erlenmeyer flask (500 ml), and after making about 150 ml with water, cool to room temperature. While mixing this solution with shaking, add hydroxyl ammonium chloride solution 5 ml and triethanolamine (1 + 4) 20 ml, further add little by little ammonium buffer solution 50 ml ⁽⁴⁾, and add potassium cyanide solution about 1 ml. After adding Thymolphthalein complexon indicator 0.05 to 0.08 g ⁽⁵⁾ to mix by shaking, immediately titrate by 0.05 mol/l EDTA standard solution, and take the point where the color of the solution has turned to yellow or colorless as the end point.

Notes ⁽⁴⁾ In the titration conditions, pH is 10.0 to 10.5, but according to this operation pH becomes about 10. If necessary, it shall be affirmed by using pH meter.

- (5) If the using amount is too large, the judgement of end point of titration becomes difficult, and therefore excess amount more than required amount shall not be added.

3.3.5 Calculation The manganese content in the sample shall be calculated according to the following formula:

$$\text{Manganese (\%)} = \frac{V \times 0.002\,747}{W} \times 100$$

where V : used amount of 0.05 mol/l EDTA standard solution (ml)

W : weighed-out amount of sample (g)

3.3.6 Analysis Precision The analysis precision according to this method shall be in accordance with Table 2.

Table 2

Manganese content % (3)	Standard deviation in a laboratory	Standard deviation between laboratories
62.59	0.112	0.195

3.4 Potentiometric Titration Method

3.4.1 Summary Decompose the sample by hydrochloric acid, hydrofluoric acid and perchloric acid, and carry out perchloric acid white fume treatment to remove hydrochloric acid and hydrofluoric acid. Let sodium diphosphate coexist, adjust pH of solution by hydrochloric acid, and titrate with potassium permanganate standard solution by using a potentiometric titration apparatus.

3.4.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1 + 2, 1 + 4)
- (3) Perchloric acid (60 %)
- (4) Hydrofluoric acid (46 %)
- (5) Sodium disulfate
- (6) Sodium diphosphate saturated solution Add warm water 1000 ml to sodium diphosphate 10 hydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) 145 g, and after dissolving by so heating as not to exceed 60°C, cool it. Prepare this solution at each using time.
- (7) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4 /l)
The preparation, standardization and preservation methods shall be in accordance with 4.4 (9) of JIS K 8001.

3.4.3 Apparatus and Devices For the apparatus and devices, generally those of the following shall be used.

Potentiometric titration apparatus The potentiometer shall be in accordance with 3.1.1 of JIS K 0113, having mV marking on pH meter may be used, and for electrodes, either one combination of the following shall be used:

- (1) Platinum - saturated calomel
- (2) Platinum - tungsten
- (3) Platinum - platinum

3.4.4 Weighing-Out Amount of Sample The weighing-out amount of sample shall be 1.0 g and weighed out to the nearest 0.1 mg.

3.4.5 Operation The determination operation shall be carried out according to the following procedures:

- (1) Preparation of Sample Solution Transfer the weighed out sample into a platinum pan (No. 200), a pan (250 ml) made of polytetrafluoroethylene, or a beaker (400 ml), and add hydrochloric acid 10 ml and perchloric acid 10 ml to decompose. Further add carefully hydrofluoric acid about 20 ml. At first gently heat, and then heat gradually strongly to generate perchloric acid white fume. Continue heating until beginning of generation of precipitate of manganese dioxide. After standing to cool, add hydrochloric acid (1 + 4) 20 ml, heat to dissolve the soluble salts, and add hot water about 50 ml ⁽²⁾.
- (2) Titration After cooling the sample obtained in (1) to ordinary temperature, transfer into a transfer flask of 250 ml and dilute with water up to the marked line. Separately take 50 ml from this solution, transfer into a beaker (500 ml) and dilute with water to 100 ml. Add sodium diphosphate saturated solution 250 ml ⁽⁶⁾, and adjust pH of this solution at 6.5 to 7.0 with hydrochloric acid (1 + 2) by using a pH meter ⁽⁷⁾. Titrate with 0.02 mol/l potassium permanganate standard solution using potentiometric titration apparatus, and take the point where the run out of potentiometer becomes maximum as the end point.

Notes ⁽⁶⁾ When sodium diphosphate is added, the precipitate of iron phosphate generates in some cases, but even the titration is carried out as it is, there is no influence.

⁽⁷⁾ In the case where the sample contains chromium, after adjusting pH of the solution at 6.5 to 7.0, and standing as it is for 30 min or more, it is titrated.

3.4.6 Calculation The manganese content in the sample shall be calculated according to the following formula:

$$\text{Manganese (\%)} = \frac{V \times 0.004395}{W \times B} \times 100$$

where V : used amount of 0.02 mol/l potassium permanganate standard solution (ml)

W : weighed-out amount of sample (g)

B : aliquot ratio of sample solution, herein 1/5

3.4.7 Analysis Precision The analysis precision according to this method shall be in accordance with Table 3.

Table 3

Manganese content % (³)	Standard deviation in a laboratory	Standard deviation between laboratories
62.49	0.099	0.122

4. Silicon Determination Method

4.1 Division of Determination Methods The determination method of silicon shall be in accordance with either one of the following:

- (1) Silicon Dioxide Gravimetric Method
- (2) Neutralization Titration Method

4.2 Silicon Dioxide Gravimetric Method

4.2.1 Summary The sample is fused by fusing mixture, added with hydrochloric acid and perchloric acid, and white-fume treated to make the silicon insoluble silicic acid. The residue is ignited and after its mass is weighed, silicon dioxide is vaporized by treating with hydrofluoric acid, and the reduced mass is weighed.

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 %)
- (4) Hydrofluoric acid (46 %)
- (5) Sulfuric acid (1 + 1, 1 + 3)
- (6) Potassium thiocyanate solution (saturated)
- (7) Fusing mixture [2 parts of sodium peroxide + 1 part of sodium carbonate (anhydrous)]

4.2.3 Weighing-Out Amount of Sample The weighing-out amount of sample shall be 0.20 g and, weighed out to the nearest 0.1 mg.