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JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical
Analysis of Ferromanganese**

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Methods for Chemical
Analysis of Ferromanganese

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1. Scope

This Japanese Industrial Standard specifies the methods for determination of manganese, carbon, silicon, phosphorus, and sulfur in ferromanganese.

2. General Items

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

3. Methods for Determination of Manganese

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

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

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 Standard:

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

3.2 Potassium Permanganate Direct Titrimetric Method

3.2.1 Summary A sample is decomposed with nitric acid and sulfuric acid and nitric acid is removed by sulfuric acid white fume treating. The sample solution is neutralized with zinc oxide and iron or the like is decomposed. The sample solution is titrated with 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) Milk of zinc oxide Zinc oxide is joined by water to make a milky solution.
- (7) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4 /l)
The methods for preparation, standardization, and storage thereof shall be in accordance with 4.4 (9) of JIS K 8001.

3.2.3 Weighing out Amount of Sample Weigh out 0.10 g of a sample to the nearest 0.1 mg.

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

- (1) Preparation of Sample Solution Transfer the weighed out sample into a beaker (300 ml), cover it with a watch glass, add 20 ml nitric acid and decompose it by heating. Add 10 ml sulfuric acid (1 + 1) thereto, evaporate it by heating and vigorously generate white fume of sulfuric acid for approx. 10 minutes. After standing to cool ⁽¹⁾, add approx. 30 ml water and dissolve soluble salts by heating ⁽²⁾.

Notes ⁽¹⁾ If there is some colored insoluble matter at that time, add approx. 5 ml hydrochloric acid (1 + 1), heat it and generate white fume again.

- ⁽²⁾ If there is some insoluble residue, filter the sample solution by using a filter paper (class 5 A) and wash it several times with warm water. Receive the filtrate and washings with a beaker (300 ml) and store it as main solution. Put the residue together with the filter paper into a platinum crucible (number 30) and incinerate them. After standing to cool, moisten it with several drops sulfuric acid (1 + 1), add approx. 1 ml hydrofluoric acid and heat it to dryness. After standing to cool, add approx. 2 g sodium disulfate and fuse it by heating. After standing to cool, put it together with the platinum crucible into the main solution preliminarily stored and dissolve the melt by heating. Wash the platinum crucible with a small amount of water and take it out.

- (2) Removal of Iron or the Like After diluting the sample solution obtained in (1) with water to approx. 100 ml, neutralize it by adding little by little milk of zinc oxide, further add a little excess amount thereof and heat it to boiling. Filter the precipitate together with excess zinc oxide by using a filter paper (class 5 A) and sufficiently wash it with warm water. Allow the filtrate and washings to become white-turbid. Receive the filtrate and washings with an Erlenmeyer flask (500 ml) and dilute it to approx. 200 ml by adding hot water. Make it white-turbid by adding 1 to 2 drops milk of zinc oxide. Discard the precipitate.
- (3) Titration After boiling the sample solution obtained in (2) by heating, immediately titrate it with 0.02 mol/l potassium permanganate standard solution and allow the point at which the pale red of supernatant does not disappear even though the solution is boiled for approx. one minute after the solution has turned pale red, to be the end point.

3.2.5 Calculation The content of manganese in a sample shall be calculated from the following formula:

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

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

W : weighing out amount of sample (g)

3.2.6 Analytical Precision The analytical precision by this method shall be as given in Table 1.

Table 1

Sample	Manganese content % ⁽³⁾	Standard deviation in the same laboratory	Standard deviation between different laboratories
High carbon ferromanganese	76.62	0.071	0.173
Low carbon ferromanganese	89.55	0.095	0.162

Note ⁽³⁾ This numerical value is the manganese content of the sample used for determination of analytical precision.

3.3 EDTA Titrimetric Method

3.3.1 Summary After decomposing a sample with nitric acid, it is acidified with hydrochloric acid and joined by hydroxylammonium chloride and triethanolamine. pH is adjusted at approx. 10. The solution is joined by potassium cyanide and titrated with EDTA standard solution utilizing 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) Sulfuric acid (1 + 1)
- (5) Potassium cyanide solution (10 g/l)
- (6) Sodium disulfate
- (7) Ammonia buffer solution After dissolving 54 g ammonium chloride with water, it is joined by 600 ml aqueous ammonia and diluted to 1000 ml with water.
- (8) Hydroxylammonium chloride solution (50 g/l)
- (9) Triethanolamine (1 + 4)
- (10) 0.05 mol/l disodium ethylenediaminetetraacetate (hereinafter, referred to as EDTA) standard solution (18.613 g $C_{10}H_{14}O_8 N_2Na_2 \cdot 2 H_2O/l$) The methods for preparation, standardization, and storage shall be in accordance with 4.4 (5) (5.2) of JIS K 8001.
- (11) Thymolphthalein Complexon (TPC) indicator 0.1 g Thymolphthalein Complexon ($C_{38}H_{44}N_2O_{12}$) is joined by 10 g potassium nitrate and thoroughly mixed by grinding in an agate mortar.

3.3.3 Weighing out Amount of Sample Weigh out 0.10 g of a sample to the nearest 0.1 mg.

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

- (1) Preparation of Sample Solution Transfer the weighed out sample into a beaker (300 ml), cover it with a watch glass, add 20 ml nitric acid and decompose it by heating. Evaporate it to dryness by successively heating and further ignite it. After standing to cool, add 10 ml hydrochloric acid (1 + 1) and dissolve soluble salts by heating ⁽²⁾.
- (2) Titration Transfer the sample solution obtained in (1) into an Erlenmeyer flask (500 ml). After diluting it to approx. 150 ml with water, cool it to room temperature. Add 5 ml hydroxylammonium chloride solution and 20 ml triethanolamine (1 + 4) with mixing this solution by shaking, further add little by little 50 ml ammonia buffer solution ⁽⁴⁾ and add approx. 1 ml potassium cyanide solution. Add 0.05 to 0.08 g Thymolphthalein Complexon indicator ⁽⁵⁾. After mixing them by shaking, immediately titrate it with 0.05 mol/l EDTA standard solution and allow the point at which the solution just has turned yellow or colourless to be the end point.

Notes (4) Though the titrating condition is 10.0 to 10.5 in pH, pH becomes approx. 10 by this operation. If necessary, it is confirmed by using a pH meter.

(5) If the use amount is much, the end point of titration becomes difficult to be judged. Therefore, excess amount more than necessary one shall not be added.

3.3.5 Calculation The content of manganese in a sample shall be calculated from the following formula:

$$\text{Manganese (\%)} = \frac{V \times 0.002747}{W} \times 100$$

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

W : weighing out amount of sample (g)

3.3.6 Analytical Precision The analytical precision by this method shall be as given in Table 2.

Table 2

Sample	Manganese content % (3)	Standard deviation in the same laboratory	Standard deviation between different laboratories
High carbon ferromanganese	76.57	0.143	0.105
Low carbon ferromanganese	89.75	0.098	0.144

3.4 Potentiometric Titration Method

3.4.1 Summary A sample is decomposed with hydrochloric acid, hydrofluoric acid and perchloric acid, and hydrochloric acid and hydrofluoric acid are removed by perchloric acid white fume treatment. Sodium diphosphate is made to coexist and pH of the solution is regulated with hydrochloric acid. The sample solution is titrated with potassium permanganate standard solution by using a potentiometric titration device.

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) Sulfuric acid (1 + 1)
- (6) Sodium disulfate

- (7) Sodium diphosphate saturated solution 145 g sodium diphosphate decahydrate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10 \text{H}_2\text{O}$) is joined by 1000 ml warm water. After dissolving it by heating so as not to exceed 60°C , the solution is cooled. This solution is prepared each service.
- (8) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4/l) The methods for the preparation, standardization, and storage shall be in accordance with 4.4 (9) of JIS K 8001.

3.4.3 Apparatus The following apparatus shall, as a rule, be used.

Potentiometric titration apparatus The potentiometer in accordance with 3.1.1 of JIS K 0113 and the pH meter with mV indication may be used and for the electrode, any combination of the following is used:

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

3.4.4 Weighing out Amount of Sample Weigh out 1.0 g of a sample to the nearest 0.1 mg.

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

- (1) Preparation of Sample Solution Transfer the weighed out sample into a beaker (300 ml), cover it with a watch glass and decompose it by adding 20 ml hydrochloric acid and 0.2 ml hydrofluoric acid. Add 10 ml perchloric acid thereto, at first gently heat it, gradually ignite it and generate white fume of perchloric acid. Continue to heat it until the viscosity of solution increases and the precipitate of manganese oxide starts to be generated. After standing to cool, add 20 ml hydrochloric acid (1 + 4), dissolve soluble salts by heating and add approx. 50 ml hot water ⁽²⁾.
- (2) Titration After cooling the solution obtained in (1) to ordinary temperature, transfer it into a transfer flask of 250 ml and dilute it to the marked line with water. Separately take 50 ml from this solution, transfer it into a beaker (500 ml) and dilute it to 100 ml with water. Add 250 ml sodium diphosphate saturated solution ⁽⁶⁾ and regulate pH of this solution at 6.5 to 7.0 with hydrochloric acid (1 + 2) using a pH meter ⁽⁷⁾. Titrate it with 0.02 mol/l potassium permanganate standard solution by using a potentiometric titration apparatus and allow the point at which the deflection of a potentiometer becomes the maximum one to be the end point.

Notes ⁽⁶⁾ When sodium diphosphate is added, the precipitate of iron phosphate is occasionally generated. However, there is no influence if continuing titration.

⁽⁷⁾ When chromium is contained in a sample, after regulating pH of solution at 6.5 to 7.0, let it stand for not less than 30 minutes and then titrate it.

3.4.6 Calculation The content of manganese in a sample shall be calculated from the following formula:

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

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

W : weighing out amount of sample (g)

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

3.4.7 Analytical Precision The analytical precision by this method shall be in accordance with Table 3.

Table 3

Sample	Manganese content % (³)	Standard deviation in the same laboratory	Standard deviation between different laboratories
High carbon ferromanganese	76.53	0.092	0.169
Low carbon ferromanganese	89.56	0.084	0.181

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:

- (1) Gas Volumetric Method This method applies to the sample of not less than 0.05 % in carbon content.
- (2) Electric Conductivity Method This method applies to the sample of not less than 0.001 % in carbon content.
- (3) Coulometric Method This method applies to the sample of not less than 0.001 % in carbon content.
- (4) Infrared Absorption Method This method shall be applied to the sample of not less than 0.001 % in carbon content.

4.2 Gas Volumetric Method

4.2.1 Summary A sample is heated in a current of oxygen, gas and carbon is thoroughly oxidized to carbon dioxide. It is, together with oxygen, collected with a buret and the volume of gas is measured. Then, carbon dioxide is absorbed with alkali solution to be removed. The residual gas volume is measured and its volumetric loss is obtained.

4.2.2 Appliance and Materials The appliance 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 Adding Amount of Combustion Improver Weigh out, as a rule, a sample in accordance with Table 4 to the nearest 0.1 mg and add combustion improver. Select the optimum combustion improver ⁽⁸⁾ from among those given in 5. (13) of JIS Z 2615 and add the amount optimum for the apparatus to be used.

Table 4

Carbon content %	Weighing out amount of sample g
0.05 and over, up to 0.3	2.0
0.3 and over, up to 1.0	1.0
1.0 and over, up to 3.0	0.50
3.0 and over, up to 6.0	0.25
6.0 and over	0.10

Note ⁽⁸⁾ Tin, copper, iron, tungsten, etc.

4.2.5 Preparing Operation The preparing operation shall be in accordance with 6.3.3 of JIS Z 2615.

Further, when a tubular electric resistance heating furnace is used, the temperature in a combustion tube shall be kept at 1200 to 1300°C ⁽⁹⁾.

Furthermore, when a high frequency induction heating furnace is used, conditions concerning high frequency induction heating ⁽¹⁰⁾ shall be set.

Notes ⁽⁹⁾ The temperature shall be corrected considering the difference between the temperature indication of a pyrometer and the temperature in a combustion tube.

⁽¹⁰⁾ Those are conditions determined correspondingly to the specifications of an apparatus to be used such as, for instance, the anode current and grid current of high frequency oscillator or the like.

4.2.6 Determination Operation The determination operation shall be as follows:

(1) In the Case of Using Tubular Electric Resistance Heating Furnace
It shall be in accordance with 6.3.4 of JIS Z 2615.

(2) In the Case of Using High Frequency Induction Heating Furnace
It shall be in accordance with 6.3 Remark of JIS Z 2615.