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Iron ores — Methods for determination of calcium content

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law. Consequently, JIS M 8221:1983 (former edition) is replaced with this Standard.

In this revision, the relevant provisions of ISO Standard are described in Annex 3, intending conformance to International Standard.

JIS M 8221 contains Annexes below:

Annex 1 (normative): Potassium permanganate titrimetric determination after separation of co-existed elements and precipitated calcium oxalate

Annex 2 (normative): Disodium dihydrogen ethylenediamine tetraacetate (disodium EDTA) titrimetric determination after separation of co-existed elements

Annex 3 (normative): Flame atomic absorption spectrometric method

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Iron Ores — Methods for determination of calcium content

Introduction In this Japanese Industrial Standard, Annex 1 specifies method for titrimetric determination with potassium permanganate of **JIS M 8221:1983**, and Annex 2 specifies Method for EDTA direct titrimetric determination of **JIS M 8221:1983** after revision respectively. Annex 3 is Japanese Industrial Standard prepared based on **ISO 10203 Iron ores — Determination of calcium content — Flame atomic absorption spectrometric method** published in 1992, without any modification in technical content and the rules for the drafting and presentation of Japanese Industrial Standard.

1 Scope This Japanese Industrial Standard specifies the methods for determination of calcium content in iron ores.

2 Normative references The following standards contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards indicated below shall be applied.

JIS K 8001 *General rule for test methods of reagents*

JIS K 8005 *Reference materials for volumetric analysis*

JIS M 8202 *Iron ores — General rules for chemical analysis*

3 General requirements General requirements common to methods for determination shall be in accordance with **JIS M 8202**.

4 Division of determination methods The method for determination of calcium content shall be in accordance with any one of the following.

- a) **Potassium permanganate titrimetric determination after separation of co-existed elements and precipitated calcium oxalate** This method is applicable to the sample of calcium content 0.1 % (*m/m*) or over up to and including 10 % (*m/m*) and in accordance with Annex 1.
- b) **Disodium dihydrogen ethylenediamine tetraacetate (disodium EDTA) titrimetric determination after separation of co-existed elements** This method is applicable to the sample of calcium content 0.1 % (*m/m*) or over up to and including 10 % (*m/m*) and in accordance with Annex 2.
- c) **Flame atomic absorption spectrometric method [Identical with International Standard (ISO 10203)]** This method is applicable to the sample of calcium content 0.01 % (*m/m*) or over up to and including 10.0 % (*m/m*) and in accordance with Annex 3.

**Annex 1 (normative) Potassium permanganate titrimetric
determination after separation of co-existed
elements and precipitated calcium oxalate**

1 Summary Decompose the sample with hydrochloric acid, nitric acid and perchloric acid, and filtrate. Separate iron in the filtrate by extracting with 4-methyl-2-pentanone. Fuse the residue with sodium disulfate after carrying out hydrofluoric acid treatment. Combine the solution to the filtrate. Neutralize this solution with ammonium chloride and ammonia water. Filtrate the precipitate of iron, aluminium and titanium. And precipitate manganese with ammonium peroxodisulfate and ammonia water, filtrate it. Then precipitate calcium as calcium oxalate with ammonium oxalate. Filter out the precipitate. Decompose the precipitate with sulfuric acid and titrate the separated oxalic acid with potassium permanganate standard solution.

2 Reagents Reagents shall be as follows:

- a) **Hydrochloric acid**
- b) **Hydrochloric acid** [10+6 (1), 1+1, 1+2, 2+100]
- c) **Nitric acid**
- d) **Perchloric acid**
- e) **Hydrofluoric acid**
- f) **Sulfuric acid** (1+1, 1+3)
- g) **Ammonia water**
- h) **Ammonia water** (1+1)
- i) **Hydrogen peroxide** (1+ 9)
- j) **Ammonium chloride**
- k) **Ammonium chloride solution** Weigh 10 g of ammonium chloride and put in a beaker (500 ml). Add 500 ml of water and dissolve it by stirring. Add ammonia water drop by drop until making the solution weak alkaline.
- l) **Ammonium peroxodisulfate**
- m) **Manganese(II) sulfate solution** (50 g/l)
- n) **Sodium disulfate**
- o) **Ammonium oxalate** Dissolve 50 g of ammonium oxalate monohydrate with water and dilute to 1 l.
- p) **4-methyl-2-pentanone**
- q) **0.02 mol/l potassium permanganate standard solution** The method of preparation, standardization and reservation of it shall be in accordance with 4.5 (7) of JIS K 8001 (0.02 mol/l potassium permanganate solution).

- r) **0.007 mol/l potassium permanganate standard solution** Weigh and take 1.1 g of potassium permanganate in a beaker (2 000 ml), dissolve it by adding 1 050 ml of water, heat gently for 1 h to 2 h and allow to stand in a dark place for one day and night. Then filter the supernatant with a sintered-glass filter (no washing before and after that), put it into the brown bottle washed by steam for approx.30 min and store it in a dark place. Obtain the factor of this solution as follows:

Accurately weigh out 0.6 g to 0.8 g of sodium oxalate (JIS K 8005) dried at 150 °C to 200 °C, hereafter carry out in accordance with 4.5 (7) of JIS K 8001 (0.02 mol/l potassium permanganate solution) and calculate the factor of the solution with the amount of titration by the following formula:

$$F_1 = \frac{G \times B}{(V_1 - V_2) \times 0.00223}$$

where, F_1 : factor of 0.007 mol/l potassium permanganate standard solution

G : mass of weighed out sodium oxalate (g)

B : aliquot ratio

V_1 : amount of 0.007 mol/l potassium permanganate standard solution used for titration of sodium oxalate solution (ml)

V_2 : amount of 0.007 mol/l potassium permanganate standard solution used for titration of blank test solution (ml)

- s) **0.017 mol/l calcium chloride standard solution** Weigh out 1.668 2 g calcium carbonate dried at 110 °C for approx. 1 h, transfer it into a beaker (300 ml), dissolve it with a small amount of hydrochloric acid, transfer it into a volumetric flask (1 000 ml) and dilute it to the mark with water. Calculate the factor of this solution as follows :

Take 30 ml of an aliquot calcium chloride standard solution, dilute the amount of solution to approx. 150 ml with warm water. Make the solution slightly alkaline with ammonia water, hereafter carry out in accordance with the procedures of 4.4 a) and 4.5. Calculate the factor of the standard solution with the following formula. Use 0.007 mol/l potassium permanganate standard solution [2 r] for titration.

$$F_2 = \frac{F_1 \times V}{30}$$

where, F_2 : factor of 0.017 mol/l calcium chloride standard solution

V : amount used for titration of 0.007 mol/l potassium permanganate standard solution (ml)

- t) **4'-dimethyl amino azobenzene-2-carbonic acid (methyl red) solution** Prepare it in accordance with 4.4 (indicator) of JIS K 8001.

Note (1) Prepare this acid solution accurately, because of using in the solvent extraction procedure.

3 Test portion Test portion shall be 1.0 g.

4 Procedure

4.1 Preparation of sample solution Preparation of sample solution shall be as follows :

- a) Weigh out and put the sample into a beaker (300 ml), cover it with a watch-glass, add 30 ml of hydrochloric acid. First, place the beaker on the frame which is the low temperature region (60 °C to 100 °C) of the hot plate and keep it as it is for approx. 1 h. Thereafter, transfer the beaker on the high temperature region, dissolve the sample by heating to near boiling for approx. 10 min. Then, add 5 ml of nitric acid and 10 ml of perchloric acid, vaporize the solution by maintaining heating for approximately 10 min under the condition in which white fume starts to generate, its inside of the beaker turns to transparent and fume of perchloric acid is refluxed along inside wall of beaker. After standing to cool, add 30 ml of hydrochloric acid (1+1) and dissolve the soluble salts by heating. Thereafter, add approx. 30 ml of warm water, mix them by shaking, filter the insoluble residue by using a filter paper (Class 5B), rub the inside walls of beaker by using a glass rod with rubber tube and transfer the adhering substances onto the filter paper. Wash the surface of filter paper with warm hydrochloric acid (2+100) until the yellow color of iron (III) chloride is no more observed on the filter paper. Then, wash it with warm water until acid is not observed in the washings. Transfer the insoluble residue together with the filter paper into a platinum crucible (No. 30) and reserve it. Receive the filtrate and washings with a beaker (300 ml).
- b) After heating to evaporate this solution and generating white fume, allow standing to cool. After dissolving the soluble salts by adding 20 ml of hydrochloric acid (10+6), transfer it into a separatory funnel (200 ml), wash the inside walls of the beaker with hydrochloric acid (10+6) and transfer it into the separatory funnel. Add a slightly exceeding amount of 4-methyl-2-pentanone than that of sample solution, vigorously mix them by shaking for approx. 1 min and allow to stand for a while. After allowing the two layers to separate, carefully take out the lower layer of aqueous solution layer into the original beaker. Further, add 5 ml of hydrochloric acid (10+6) to the organic phase in the separatory funnel and vigorously mix them again by shaking for approx. 10 s. When the solution is separated into two layers after standing still for a while, take out the lower layer of aqueous solution phase, add it to the original beaker and discard the upper layer of organic phase. Boil it for approx. 5 min by heating and vaporize most of organic solvent. Thereafter, add 5 ml of nitric acid and 10 ml of perchloric acid, continue to heat and evaporate it until thick white fume is generated. Allow standing to cool, dissolve the salts by adding approx. 50 ml of warm water and boil it for several min. Thereafter, take it down from the heat source and reserve it as a main solution.
- (c) After drying the insoluble residue reserved in a), incinerate it by ignition and allow to cool it. Moisten the ignited residue with sulfuric acid (1+1), add approx. 5 ml of hydrofluoric acid, and heat gently to vaporize silicon dioxide and sulfuric acid. Af-

ter cooling, add approx. 3 g of sodium disulfate, cover a lid and fuse the residue by first heating cautiously and gradually rising the temperature to be heated dark red hot state. After cooling, put the platinum crucible as it is into the main solution reserved in b), add 5 ml of hydrochloric acid and dissolve the melt by gently heating. Wash the platinum crucible with warm water and take it out.

4.2 Hydroxide Separation The hydroxide separation shall be in accordance with either of the following:

a) Sample under 2.5 % (*m/m*) in Aluminium content

- 1) Add water to the sample solution obtained in 4.1 and dilute the solution to approx. 100 ml. Add approx. 3 g of ammonium chloride, and dissolve it by stirring. Add 2 to 3 drops of methyl red solution [2 t)] as an indicator, neutralize the solution by dripping ammonia water (1+1), while stirring the solution, until the solution changes into yellow, and generate the precipitate of hydroxide. Heat this precipitate gradually and take it down from the heat source after boiling for approx. 2 min. After the precipitate has settled, filter it by using a filter paper (Class 5 A), wash it several times with warm ammonium chloride solution [2 k)] heated to approx. 40 °C to 60 °C and put the filtrate and washings into a beaker (300 ml).
- 2) Discard the precipitate.

b) Sample 2.5 % (*m/m*) or over in aluminium content

- 1) Preserve the solution obtained in accordance with the procedures of a) 1).
- 2) Wash out the precipitate into the original beaker by spraying water through the funnel as it has filter paper fitted, add 10 ml of hydrochloric acid and dissolve it by heating. Filter it by using the original filter paper and wash it first 3 times with hot hydrochloric acid (1+2) heated to 60 °C or higher, then several times with warm hydrochloric acid (2+100) heated to approx. 40 °C to 60 °C and at last with warm water until acid is no more observed in the washings. Dilute the amount of solution to approx. 100 ml. Hereafter, carry out in accordance with the procedures of a) 1) "adding of ammonium chloride" and join obtained solution with preserved solution in b) 1). Discard the precipitate

4.3 Separation of manganese The separation of manganese shall be as follows:

(a) Sample under 5 % (*m/m*) in manganese content

- 1) Heat to evaporate the filtrate and washings obtained in 4.2 to approx. 150 ml ⁽²⁾. Add 1 g of ammonium peroxodisulfate into the solution with stirring, then add 25 ml of ammonia water and maintain heating. Decompose ammonium peroxodisulfate by boiling for approx. 10 min and precipitate manganese. Then, filter the precipitate by using a filter paper (Class 5 B), wash it several times with warm water. Put the filtrate and washings into a beaker (500 ml).
- 2) Discard the precipitate.

Note ⁽²⁾ If precipitate is generated in that case, filter it by using a filter paper (Class 5 A), wash it several times with warm ammonium chloride solution [2 k] heated to approx. 40 °C to 60 °C, put the filtrate and washings into a beaker (300 ml). Heat to evaporate the filtrate and washings to approx. 150 ml. Discard the precipitate.

(b) Sample 5 % (m/m) or over in manganese content

- 1) Preserve the solution obtained in accordance with the procedure of a) 1).
- 2) Wash out the precipitate into the original beaker by spraying water through the funnel as it has the filter paper attached, dissolve the precipitate by adding little by little warm hydrochloric acid (1+2) heated to approx. 40 °C to 60 °C and hydrogen peroxide (1+9) and wash it with warm water until acid no more observed in the washings. Thereafter, neutralize the solution with ammonia water. Hereafter, carry out in accordance with the procedures of a) 1) "adding of ammonium peroxodisulfate" while stirring the solution, and join obtained solution with preserved solution in b) 1). Discard the precipitate.

4.4 Generation of precipitate Generation of the precipitate shall be in accordance with either of the following.

(a) Sample 0.2 % (m/m) or over in calcium content

- 1) Heat to evaporate the filtrate and washings obtained in 4.3 to approx. 150 ml, make the solution slightly alkaline, continue to heat it by boiling. Add 15 ml of ammonium oxalate monohydrate solution into the solution with stirring.
- 2) Allow to stand at 70 °C to 80 °C for approx. 1 h and digest the precipitate. Filter the precipitate solution through the filter paper (Class 5 B), wash it approx. 10 times with warm water. Discard the filtrate and washings.

(b) Sample under 0.2 % (m/m) in calcium content

- 1) Carry out in accordance with the procedure of a) 1).
- 2) After boiling the solution for 2 min to 3 min, allow to stand at 70 °C to 80 °C for approx. 1 h or longer, or accurately add 5 ml of 0.017 mol/l calcium chloride standard solution [2 s], allow to stand at 70 °C to 80 °C for approx. 1 h or longer and digest the precipitate. Filter the precipitate by using a filter paper (Class 5 B), wash it approx. 10 times with warm water. Discard the filtrate and washings.

4.5 Titration Wash out the precipitate obtained in 4.4 a) or 4.4 b) through a small hole opened of the filter paper into a beaker (500 ml) with spraying water. Wash the filter paper first with 30 ml of warm hydrochloric acid (1+3) heated to approx. 40 °C to 60 °C and then wash it with warm water until acid is no more observed in the washings. Dilute the solution to approx. 200 ml by adding warm water, and heat it at approx. 80 °C. For the precipitate obtained in 4.4 a), titrate with 0.02 mol/l potassium permanganate standard solution [2 q] or for the precipitate obtained in (4.4 b), titrate with 0.007 mol/l potassium permanganate standard solution [2 r] ⁽³⁾. In the both titrations,

allow the point at which the solution turns faint red by final one drop of standard solution to be the end point. And obtain the amounts of titration of potassium permanganate standard solution.

Note ⁽³⁾ In that case, if several ml of manganese (II) sulfate solution is added in titration operation, the titration will be carried out by the fast reaction from the beginning stage.

5 Blank test In parallel with the same procedures of the sample solution in accordance with 4.1 to 4.5, carried out the blank test by using only reagents without the sample.

6 Calculation The calcium content shall be calculated as follows:

a) Calculate the calcium content in the sample from the amounts of titration obtained in 4.5 and 5 with each of the following formulas.

1) For the precipitate obtained in 4.4 a)

$$C_a = \frac{(V_1 - V_2) \times 0.002\ 004}{m} \times 100$$

where, C_a : calcium content in the sample [% (m/m)]

V_1 : consumed amounts of 0.02 mol/l potassium permanganate standard solution for the titration of the sample solution (ml)

V_2 : consumed amounts of 0.02 mol/l potassium permanganate standard solution for the titration of the blank test solution (ml)

m : test portion (g)

2) For the precipitate obtained in 4.4 b)

$$C_a = \frac{(V_3 - V_4 - V_5) \times 0.000\ 68}{m} \times 100$$

where, C_a : the same as a) 1)

V_3 : consumed amounts of 0.007 mol/l potassium permanganate standard solution for the titration of the sample solution (ml)

V_4 : consumed amounts of 0.007 mol/l potassium permanganate standard solution for the titration of the blank test solution (ml)

V_5 : added amounts of 0.017 mol/l calcium chloride standard solution (ml) ⁽⁴⁾

m : the same as a) 1)

Note ⁽⁴⁾ In that case, 0.017 mol/l calcium chloride standard solution does not used for the procedure of 4.4 b), V_5 shall be zero.