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JAPANESE INDUSTRIAL STANDARD

Methods for Chemical

Analysis of Gypsum

JIS R 9101-1986



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Methods for Chemical Analysis of Gypsum

R 9101-1986

1. Scope

This Japanese Industrial Standard specifies the methods for chemical analysis of natural gypsum, chemical gypsum, and calcined gypsum.

2. Items of Analysis

The items of analysis specified in this standard shall be as follows:

- | | |
|---|---|
| (1) Water content | (f.w.) |
| (2) Combined water | (c.w.) |
| (3) Silicon dioxide + insoluble residue | (SiO ₂ +insol.) |
| (4) Aluminum oxide + iron (III) oxide | (Al ₂ O ₃ +Fe ₂ O ₃) |
| (5) Iron (III) oxide | (Fe ₂ O ₃) |
| (6) Calcium oxide | (CaO) |
| (7) Magnesium oxide | (MgO) |
| (8) Sulfur trioxide | (SO ₃) |
| (9) Sulfur dioxide | (SO ₂) |
| (10) Carbon dioxide | (CO ₂) |
| (11) Sodium oxide and potassium oxide | (Na ₂ O, K ₂ O) |
| (12) Fluorine | (F) |
| (13) Total phosphoric acid | (t.P ₂ O ₅) |
| (14) Water-soluble phosphoric acid | (sol.P ₂ O ₅) |
| (15) Chlorine | (Cl) |
| (16) Free acid | (f.H ₂ SO ₄) |
| (17) pH | |

Applicable Standards: See page 59.

3. Preparation and Storage of Sample

Samples shall be taken up and prepared according to the following, and be stored in an air-tight container free of the influence from the open air.

- (1) Natural Gypsum Carry out sampling according to JIS M 8100, and pulverize it as fine as 5 mm size, or smaller in the case of the determination of water content, and as fine as completely passing through 250 μm ⁽¹⁾ mesh of a standard sieve specified in JIS Z 8801 in the case of the analysis sample for items other than water content.

If the sample taken is not suitable for reducing by crushing, carry out suitable predrying by natural drying or by an air bath maintained at 45°C or under. Record, however, the loss on predrying by weighing the mass of sample before and after predrying operation in the case of water content determination.

In the case of analysis sample for items other than water content, spread crushed and reduced sample on a suitable dish as thin layer, and dry it in an air bath controlled at 45°C until getting a constant weight.

$$a = \frac{m_1 - m_2}{m_1} \times 100$$

where a : loss on predrying (%)

m_1 : mass of sample before predrying (g)

m_2 : mass of sample after predrying (g)

Note (1) If there is no assurance of uniformity of sample by using a 250 μm sieve, use the analysis sample that has passed completely through a 149 μm sieve.

- (2) Chemical Gypsum Carry out sampling and preparation according to 3. (1).
- (3) Calcined Gypsum Let the sample prepared according to 2. in JIS R 9112 be the sample for the determination of water content. After drying this sample in an air bath controlled at 45°C until getting a constant weight, use this dried one as analysis sample for items other than water content.

4. General Items

General items that are in common to chemical analysis shall, as a rule, conform to the specifications in JIS K 0050, JIS K 0115, JIS K 0121, JIS K 0122, and JIS Z 8802.

5. Arrangement of Results of Analysis

5.1 The methods of arrangement of analysis values shall be as follows.

- (1) Water content shall be expressed by percent ratio to the mass of supplied sample as it is, and rounded to the first decimal place according to JIS Z 8401.
- (2) Combined water, calcium oxide, and sulfur trioxide shall be expressed by percentage to the mass of dried sample, and rounded off to the first decimal place according to JIS Z 8401.
- (3) Silicon dioxide+insoluble residue, aluminum oxide+iron (III) oxide, iron (III) oxide, magnesium oxide, sulfur dioxide, carbon dioxide, sodium oxide, potassium oxide, fluorine, total phosphoric acid, water-soluble phosphoric acid, chlorine, and free acid shall be expressed by percentage to the mass of dried sample, and rounded off to the second decimal place according to JIS Z 8401.
- (4) The value of pH shall be rounded off to the first decimal place according to JIS Z 8401.

5.2 When carrying out the analysis, every operation shall be supported by the blank test by which measured value shall be corrected.

6. Determination of Water Content

6.1 Classification of Methods The determination of water content shall be carried out according to gravimetric method. There is, however, a difference on the mass of sample between the cases of natural gypsum and chemical gypsum, and the case of calcined gypsum.

6.2 Summary. Weigh the loss of mass on drying when the weight of sample dried at 45°C has become a constant weight, and find the adhesion percentage of water.

6.3 Natural Gypsum and Chemical Gypsum

6.3.1 Weighing-Out quantity of Sample Weigh accurately about 200 g of the sample to the nearest 0.1 g.

6.3.2 Operation Determinating operation shall be as follows:

- (1) Weigh the sample in a suitable drying dish whose mass has been weighed in advance, and spread it as thin as possible to be dried easily. Dry it for two hours in an air bath controlled at 45°C, and, after cooling, weigh its mass.

- (2) Repeat the drying operation respectively for one hour, and find the loss on drying when the difference between two masses after and before drying of one hour has become 0.5 g or less.

6.3.3 Calculation Adhesion percentage of water in the sample shall be calculated according to the following formula (1) or (2).

- (1) In the case of no predrying when preparing sample.

$$f.w. = \frac{m}{s} \times 100$$

where $f.w.$: adhesion percentage of water (%)

m : loss of mass (g)

s : mass of sample weighed out in 6.3.1 (g)

- (2) In the case of predrying when preparing sample.

$$f.w. = a + \frac{m}{s} \times (100 - a)$$

where $f.w.$: adhesion percentage of water (%)

a : loss on predrying obtained in 3.(1) (%)

m : loss of mass (g)

s : mass of sample weighed out in 6.3.1 (g)

6.4 Calcined Gypsum

6.4.1 Quantity of Sample Weigh out accurately about 10 g of the sample to the nearest 0.01 g.

6.4.2 Operation Determination operation shall be as follows:

- (1) Weigh the sample in a flat weighing bottle (60 mm x 30 mm) whose mass has been weighed in advance, and dry it for two hours in an air bath controlled at 45°C. After cooling, weigh its mass.
- (2) Repeat the drying operation respectively for one hour, and find the loss on drying when the difference between two masses after and before drying of one hour has become 0.02 g or less.

6.4.3 Calculation Adhesion percentage of water in the sample shall be calculated according to the following formula:

$$f.w. = \frac{m}{s} \times 100$$

where $f.w.$: adhesion percentage of moisture (%)

m : loss of mass (g)

s : mass of sample weighed out in 6.4.1 (g)

7. Determination of Combined Water

7.1 Classification of Method The determination of combined water shall be carried out according to gravimetric method.

7.2 Summary Weigh the loss of mass by heating when the mass of the sample heated at 240 to 260°C has become a constant quantity, and find the content percentage of combined water.

7.3 Weighing-Out Quantity of Sample Weigh accurately about 1.0 g of the sample to the nearest 0.1 mg.

7.4 Operation Determination operation shall be as follows:

- (1) Weigh out the sample into a cylindrical weighing bottle (30 mm x 45 mm) whose mass has been weighed in advance, and, after putting loosely a cap, heat it for about one hour in an electric furnace controlled at 240 to 260°C. After cooling, weigh its mass.
- (2) Repeat heating respectively for 30 minutes, and find a loss on heating when a constant weight has been obtained.

7.5 Calculation The content percentage of the combined water in the sample shall be calculated according to the following formula:

$$c.w. = \frac{m}{s} \times 100$$

where $c.w.$: content percentage of combined water (%)

m : loss on heating (g)

s : mass of sample weighed out in 7.3 (g)

8. Determination Method of Silicon Dioxide+Insoluble Residue

8.1 Classification of Method The determination of silicon dioxide+insoluble residue shall be carried out according to a gravimetric method.

8.2 Summary After dissolving sample in hydrochloric acid and perchloric acid, dehydrate silicon dioxide by heating to make it insoluble, and filtrate them to separate the insolubles. Heat strongly the precipitate of silicon dioxide+insoluble residue, and then weigh its mass.

8.3 Reagent Reagents shall be as follows:

- (1) Hydrochloric acid (1+1)
- (2) Perchloric acid (60%)

8.4 Weighing-Out Quantity of Sample Weigh out accurately about 1.0 g of the sample to the nearest 0.1 mg.

8.5 Operation Determination operation shall be in accordance with the following procedures:

- (1) Weigh out the sample into a beaker (200 ml), and, after making them slurry state ⁽²⁾ by adding a little of water, pour little by little 5 ml of hydrochloric acid (1+1) from the rim of the beaker covered with a watch glass.
- (2) Removing the watch glass, add 5 ml of perchloric acid (60%) to mix well with stirring, and heat them on a sand bath ⁽³⁾. When dense white fume of perchloric acid rises, cover the beaker again with a watch glass, and heat on for successively ten minutes.
- (3) After removing the beaker from the sand bath and cooling, add 5 ml of hydrochloric acid (1+1) and about 50 ml of warm water, and after mixing with stirring, heat it for about 15 minutes on a water bath. While the operation, stir it sometimes, and make soluble components completely dissolve by crushing lumps with the tip of a glass rod.
- (4) Filtrate it through a filter paper (Class 5 B), and wash sufficiently with warm water ⁽⁴⁾. Place the filtrate and washings in a beaker (300 ml), and, after cooling to room temperature, transfer it to a 250 ml measuring flask with rinsing the beaker, and then dilute with water up to the marked line.

Make this solution the sample solution (A), and use for the determination of aluminum oxide+iron (III) oxide, iron (III) oxide, magnesium oxide, sodium oxide and potassium oxide, total phosphoric acid, and others.

- (5) After drying the insolubles which are put in a porcelain crucible together with the filter paper, under loosely covering with a cap, incinerate the filter paper by gradually heating with care lest the paper should flame up, and then ignite for one hour in an electric furnace controlled at $1000 \pm 50^{\circ}\text{C}$. After cooling in a desiccator, weigh the mass.

- Notes (2) In the case of the sample containing fluorine, make the sample slurry state by adding about 1 g of boric acid and about 20 ml of water, and, after preventing evaporating of silicon tetrafluoride by dissolving boric acid by means of heating, carry out the operation to add hydrochloric acid.
- (3) The temperature of the sand bath shall preferably controlled at 180 to 200°C when a thermometer is inserted in near the centre of sand.
- (4) An insufficient washing may cause the scattering of the filter paper when incinerating. Especially, in the case of a large quantity of the insolubles, close attention is needed.

8.6 Calculation The content percentage of silicon dioxide+insoluble residue in the sample shall be calculated according to the following formula:

$$\text{SiO}_2 + \text{insol.} = \frac{m}{s} \times 100$$

where $\text{SiO}_2 + \text{insol.}$: content percentage of silicon dioxide+insoluble residue (%)

m : mass of insoluble matter (g)

s : mass of sample weighed out in 8.4 (g)

9. Determination Method of Aluminum Oxide+Iron (III) Oxide

9.1 Classification of Method The determination of aluminum oxide+iron (III) oxide shall be carried out according to a gravimetric method.

9.2 Summary Making use of the sample solution (A) stored in 8.5 (4), by adding ammonium chloride and aqueous ammonia, precipitate aluminum together with iron and others, and filtrate them. Ignite the precipitate, and, after weighing the mass, calculate the content percentage of aluminum oxide+iron (III) oxide.

Remark: In cases where the sample contains phosphoric acid, titanium or others, these to precipitate.

9.3 Reagent Reagents to be used shall be as follows:

- (1) Nitric acid
- (2) Ammonium chloride saturated solution
- (3) Aqueous ammonia (1+1)
- (4) Ammonium nitrate washing solution ⁽⁵⁾ (2 W/V%)
- (5) Methyl Red indicator Dissolve 0.2g of Methyl Red in 100 ml of ethyl alcohol (95 V/V %)

Note ⁽⁵⁾ The ammonium nitrate washing solution shall be used whose color, after dropping a few drops of Methyl Red, has turned to yellow from red by adding of aqueous ammonia (1+1). If the color of this solution is returned to red again by heating, the solution whose color is changed to yellow by further dropping aqueous ammonia (1+1), is used.

9.4 Operation Determination operation shall be in accordance with the following procedures:

- (1) Separately take accurately a suitable volume aliquot ⁽⁶⁾ from the sample solution (A) stored in 8.5 (4) into a beaker (300 ml), and, after adding a few drops of nitric acid, boil several minutes.
- (2) After adding 10 ml of ammonium chloride saturated solution and a few drops of Methyl Red, add aqueous ammonia (1+1) with stirring until the color of the solution turns yellow from red, and add excessively a few drops.
- (3) After boiling a few minutes by heating, take the solution off from the heat source, and filtrate through a filter paper (5 grade A) immediately after the precipitate settles down. Wash the precipitate about 8 times with ammonia nitrate warm washing solution.
- (4) After drying the precipitate that is put in a porcelain crucible together with the filter paper, under loosely covering with a cap, incinerate the filter paper by gradually heating with care lest the paper should flame up, and then ignite for one hour in an electric furnace controlled at $1000 \pm 50^{\circ}\text{C}$. After cooling in a desiccator, weigh the mass.

Note ⁽⁶⁾ The volume of an aliquot from the sample solution (A) may preferably be 100 ml.

9.5 Calculation The content percentage of aluminum oxide+iron (III) oxide in the sample shall be calculated according to following formula:

$$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = \frac{m}{s} \times \frac{250}{v} \times 100$$

where $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$: content percentage of aluminum oxide+iron (III) oxide (%)

m : mass of precipitate (g)

s : mass of sample weighed out in 8.4 (g)

v : volume of aliquot from sample solution (A) (ml)

10. Determination of Iron (III) Oxide

10.1 Classification of Method Determination of iron (III) oxide shall be carried out according to either one of the following methods:

- (1) EDTA Titration Method This method is suitable for the sample containing 0.1% or more content of iron (III) oxide.
- (2) 1,10-Phenanthroline Absorptiometry
- (3) Atomic Absorption Analysis This method is suitable for the sample containing 1.0% or less of iron (III) oxide.

10.2 EDTA Titration Method

10.2.1 Summary After making pH of the sample solution (A) stored in 8.5 (4) to be from 2.2 to 2.5, titrate the solution with EDTA standard solution by using salicylic acid as the indicator.

10.2.2 Reagents Reagents to be used shall be as follows:

- (1) Ammonium Acetate Solution (25 W/V%)
- (2) Hydrochloric Acid (1+1)
- (3) Sodium Hydroxide Solution (10 W/V%)
- (4) Salicylic Acid Solution (2 W/V%) Dissolve 2 g of salicylic acid in 100 ml of methyl alcohol (95 V/V%).
- (5) EBT indicator Dissolve 0.2 g of Eriochrome Black T in the mixture of 15 ml of triethanol amine and 5 ml of ethyl alcohol (95 V/V%), and store in a brown bottle with a dropping pipet.

- (6) Buffer Solution (pH 10) Dissolve 70 g of ammonium chloride in a suitable amount of water, and, after adding 570 ml of aqueous ammonia, dilute with water up to 1 l.
- (7) M/100 Zinc Standard Solution Weigh out accurately about 0.65 g of zinc (⁷) to the nearest 0.1 mg in a beaker (200 ml) and, after adding 20 ml of hydrochloric acid (1+1), warm gently to dissolve the zinc completely. Transfer the solution to a 1 l measuring flask with rinsing the beaker, and, after cooling, dilute with water up to the marked line.

Calculate the factor of this standard solution according to following formula, and round off to the third decimal place.

$$f_1 = \frac{m}{0.6538}$$

where f_1 : factor of M/100 zinc standard solution

m : mass of zinc weighed out (g)

- (8) M/100 EDTA Standard Solution Dissolve 3.72 g of disodium ethylenediaminetetraacetic acid dihydrate in a suitable amount of water, and transfer it into a 1 l measuring flask. After diluting with water up to the marked line, store the solution in a polyethylene bottle. Standardize this standard solution as follows:

Separately take accurately a 25 ml aliquot of M/100 zinc standard solution into a beaker (200 ml), and dilute with water up to about 100 ml. After adding sodium hydroxide solution (10 W/V%) to neutralize it, control its pH at 9.5 to 10.0, and add 2 ml of buffer solution and a few drops of EBT indicator, then, titrate the solution with M/100 EDTA standard solution, and take such point as the end point when the color of the solution turns to clear green color from reddish purple by vanishing completely pinkish tint.

Calculate the factor of this standard solution according to the following formula, and round off to the sixth decimal place.

$$f_2 = \frac{0.0005608 \times 25 \times f_1}{v}$$

where f_2 : factor of M/100 EDTA standard solution

v : required volume of M/100 EDTA standard solution (ml)

f_1 : factor of M/100 zinc standard solution

Note (7) Make use of zinc specified in JIS K 8005 after keeping it for 24 hours or more in a calcium chloride desiccator or sulfuric acid desiccator. If there is a fear that the surface of zinc may be oxidized, use after washing successively hydrochloric acid (1+1), water and acetone and after drying for 5 minutes at 110°C.

10.2.3 Operation Determination operation shall be in accordance with the following procedures:

- (1) Take separately accurately a 100 ml aliquot from the sample solution (A) stored in 8.5 (4) into a beaker (300 ml). Add 10 ml of ammonium acetate solution (25 W/V%), and adjust its pH to be 2.2 to 2.5 by using hydrochloric acid (1+1).
- (2) After adding 1 ml of salicylic acid solution (2 W/V%) as indicator, titrate the solution with M/100 EDTA standard solution, and take as end point the point when the color of the solution turns to colorless or pale yellow from reddish purple.

10.2.4 Calculation The content percentage of iron (III) oxide in the sample shall be calculated according to the following formula:

$$\text{Fe}_2\text{O}_3 = \frac{v_1 \times f_2 \times 0.0007985}{s} \times \frac{250}{v_2} \times 100$$

where Fe_2O_3 : content percentage of iron (III) oxide (%)

v_1 : used volume of M/100 EDTA standard solution (ml)

f_2 : factor of M/100 EDTA standard solution

s : mass of sample weighed out in 8.4 (g)

v_2 : volume of aliquot taken from the sample solution (A) (ml)

10.3 1,10-Phenanthroline Absorptiometry

10.3.1 Summary After reducing the iron in the sample solution (A) stored in 8.5 (4) by ascorbic acid, add 1,10-phenanthroline, and color the solution by adjusting pH with ammonium acetate. Measure the absorbance of this solution to obtain the content percentage of iron (III) oxide.

10.3.2 Reagents Reagents to be used shall be as follows:

- (1) Ascorbic Acid Solution (5 W/V%) Store the solution in a dark and cold place, and, when coloring while storing, renew the solution.

- (2) 1,10-Phenanthroline Solution Dissolve 1 g of 1,10-phenanthroline hydrochloride monohydrate in a suitable amount of water, and dilute up to 1 l. Store in a dark and cold place, and, when coloring while storing, renew the solution.
- (3) Ammonium Acetate Solution (20 W/V%)
- (4) Hydrochloric Acid (1+1)
- (5) Iron (III) Oxide Standard Stock Solution (0.10 mg Fe₂O₃/ml)
(⁸) Weighout 0.700 g of metallic iron (99.9% or more) into a beaker (200 ml), and, after covering with a watch glass, dissolve in 20 ml of hydrochloric acid (1+1) by gentle heating. After cooling, remove the watch glass by rinsing with water, and transfer it into a 1 l measuring flask, dilute with water up to the marked line. Make this solution stock solution (1.0 mg Fe₂O₃/ml). When using it, pipet accurately a 100 ml aliquot from the stock solution into 1 l measuring flask, and dilute with water to reach a marked line. Make this solution iron (III) oxide standard stock solution (0.10 mg Fe₂O₃/ml).

Note (⁸) The standard stock solution on market whose concentration has been known may be used for this purpose.

10.3.3 Apparatus Absorptiometry analyzer shall be used.

10.3.4 Operation Determination operation shall be in accordance with the following procedures:

- (1) Separately take accurately a suitable amount of aliquot (⁹) from the sample solution (A) stored in 8.5 (4) in a 100 ml measuring flask, and dilute with water up to about 50 ml.
- (2) Add 2 ml of ascorbic acid solution (5 W/V%), mix by stirring, and further add 10 ml of 1,10-phenanthroline solution and 10 ml of ammonium acetate solution (20 W/V%). After diluting with water up to the marked line, shake it to mix, and allow it stand for 30 minutes.

- (3) Take a portion of this solution in the absorption cell of an absorptiometry analyzer, and measure its absorbance in the vicinity of 510 nm wavelength.

Note (9) The volume of an aliquot from the sample solution (A) shall be as following Table 1 according to the content of iron (III) oxide.

Table 1 Volume of Aliquot from Sample Solution

Content of iron (III) oxide %	Volume of aliquot ml
Less than 0.15	50
0.15 or more to 0.30 excl.	25
0.30 or more to 0.75 excl.	10
0.75 or more to 1.50 excl.	5

10.3.5 Preparation of Working Curve After diluting accurately 10 times with water the iron (III) oxide standard stock solution (0.10 mg Fe₂O₃/ml) prepared in 10.3.2 (5), take stepwise 0 to 30.0 ml of the solution (0 to 0.30 mg as Fe₂O₃) into 100 ml measuring flasks and dilute them with water to make respectively about 50 ml. Measure their absorbances according to the operation shown in 10.3.4 (2) and (3), and prepare the working curve by preparing the relation curve between the absorbances and the concentrations of iron (III) oxide.

10.3.6 Calculation Use the working curve prepared in 10.3.5, obtain the concentration of iron (III) oxide from the absorbance measured in 10.3.4, and calculate the content percentage of iron (III) oxide in the sample according to the following formule.

$$\text{Fe}_2\text{O}_3 = \frac{C \times 10^{-3}}{s} \times \frac{250}{v} \times 100$$

where Fe₂O₃: content percentage of iron (III) oxide (%)

C: concentration of iron (III) oxide obtained from absorbance (mg/100 ml)

s: mass of sample weighed out in 8.4 (g)

v: volume of aliquot taken from sample solution (A) (ml)

10.4 Atomic Absorption Analysis Method

10.4.1 Summary Measure the absorbance of iron which is contained in the sample solution (A) stored in 8.5 (4) by using an atomic absorption analyzer, and obtain the content percentage of iron (III) oxide.

10.4.2 Reagents Reagents to be used shall be as follows:

- (1) Hydrochloric Acid (1+1)
- (2) Perchloric Acid (60%)
- (3) Sulfuric Acid
- (4) Calcium Carbonate (for Alkali Analysis)
- (5) Matrix Solution-I Weigh out 11.6 g of calcium carbonate (for alkali analysis) into a beaker (500 ml), and disperse it in a suitable amount of water. Covering with a watch glass, dissolve by 200 ml of hydrochloric acid (1+1) that is poured in little by little from the rim of the beaker. Add 100 ml of perchloric acid (60%), and after standing it, transfer in a 1 l measuring flask, dilute with water up to the marked line. Store this solution in a polyethylene bottle.
- (6) Matrix Solution-II Dissolve 6.5 ml of sulfuric acid in a suitable amount of water, and, after standing it to cool down, transfer into a 1 l measuring flask, dilute with water up to the marked line. Store this solution in a polyethylene bottle.
- (7) Iron (III) Oxide Standard Stock Solution (1.0 mg Fe₂O₃/ml) This is the stock solution prepared in 10.3.2 (5).

10.4.3 Apparatus Atomic absorption analyzer shall be used.

10.4.4 Operation Determination operation shall be carried out according to the following procedures:

Take separately and aliquot from the sample solution (A) stored in 8.5 (4), and dilute accurately twice. Spray a portion of this solution into the air-acetylene flame of an atomic absorption analyzer, and, by using the light source for iron, measure the absorbance at 248.3 nm wavelength.

10.4.5 Preparation of Working Curve After diluting accurately 10 times with water the iron (III) oxide standard stock solution (1.0 mg Fe₂O₃/ml) prepared in 10.4.2 (7), place stepwise its 0 to 20 ml (0 to 2.0 mg as Fe₂O₃) into 100 ml measuring flasks, and dilute them with water up to respectively about 50 ml. To each of these solutions, add 10 ml (¹⁰) of matrix solution-I in 10.4.2 (5) and 10 ml (¹¹) of matrix solution-II in 10.4.2 (6), and dilute with water up to the marked line. Spray these standard solutions into the air-acetylene flame of an atomic absorption analyzer, and measure the absorbance at 248.3 nm wavelength. Prepare the working curve by plotting the relations between the absorbances and the concentrations of iron (III) oxide.

Notes (10) In the case where the content percentage (%) of calcium oxide (CaO) in the sample is already known, the volume of matrix solution-I shall be calculated according to the following formula:

$$\text{Volume to be added (ml)} = \frac{\text{CaO (\%)}}{32.6} \times 10$$

(11) In the case where the content percentage (%) of sulfur trioxide (SO₃) in the sample is already known, the volume of matrix solution-II shall be calculated according to the following formula:

$$\text{Volume to be added (ml)} = \frac{\text{SO}_3 (\%)}{46.5} \times 10$$

10.4.6 Calculation Use the working curve prepared in 10.4.5, obtain the concentration of iron (III) oxide from the absorbance measured in 10.4.4, and calculate the content percentage of iron (III) oxide in the sample according to the following formula.

$$\text{Fe}_2\text{O}_3 = \frac{C \times 10^{-3}}{s} \times \frac{250 \times 2}{100} \times 100$$

where Fe₂O₃: content percentage of iron (III) oxide (%)

C: concentration of iron (III) oxide obtained from absorbance (mg/100 ml)

s: mass of sample weighed out in 8.4 (g)

11. Determination of calcium oxide

11.1 Classification of Method Determination of calcium oxide shall be carried out according to either one of following methods:

- (1) EDTA Titration Method
- (2) Potassium Permanganate Titration Method

11.2 EDTA Titration Method

11.2.1 Summary Dissolve the sample in hydrochloric acid, and filtrate. After making pH of this solution 12.7 to 13.2, titrate it with EDTA standard solution by using NN indicator.

11.2.2 Reagents Reagents to be used shall be as follows:

- (1) Hydrochloric Acid (1+1)
- (2) Triethanolamine (1+1)
- (3) Potassium Hydroxide Solution (20 W/V%)

- (4) NN Indicator Pulverize uniformly the mixture of 0.5 g of 2-hydroxy-1-(2'-hydroxy-4'-sulfo-1'-naphthylazo)-3-naphthoic acid and 50 g of potassium sulfate, and store in a brown bottle.
- (5) M/100 EDTA Standard Solution This is the solution prepared in 10.2.2 (8).

11.2.3 Quantity of Sample Weigh out accurately about 1.0 g of the sample to the nearest 0.1 mg.

11.2.4 Operation Determination operation shall be in accordance with the following procedures:

- (1) Weigh out the sample into a beaker (200 ml), and add 20 ml of hydrochloric acid (1+1) and about 100ml of water. After dissolving soluble matter by boiling for several minutes, filtrate the solution through a filter paper (class 5 B) ⁽¹²⁾, and wash 8 times with warm water.
- (2) After cooling, transfer the filtrate and washings to a 500 ml measuring flask, and dilute it with water up to the marked line. Make this solution sample solution (B), use this for the determination of calcium oxide, magnesium oxide, and sulfur trioxide.
- (3) Separately take accurately a 25 ml aliquot from the sample solution (B) into a beaker (300 ml), and dilute with water up to 100 ml. Add 2 ml of triethanolamine (1+1) and a suitable amount of potassium hydroxide solution (20 W/V%), and, after sufficient agitation to mix, adjust pH at 12.7 to 13.2, and stand still for 2 to 3 minutes. After adding about 0.1 g of NN indicator, titrate this solution with M/100 EDTA standard solution, and take as the end point when the color of the solution turns clear blue from reddish purple after complete vanishing red tint ⁽¹³⁾ ⁽¹⁴⁾.

Notes ⁽¹²⁾ When fine particles may pass through the filter paper, filtrate the solution after boiling a little while with mixing a little amount of powdered filter paper.

⁽¹³⁾ The end point of the titration is found easily by observing through light of a tungsten lamp.

- (14) In the case of an existence of magnesium, the blue color that has first colored may recover an original color. In such case, the point of the first coloring of blue should be decided as an end point.

If a lot of magnesium exists in the solution, the recognition of the end point may become difficult. In such case, the following is advisable; at first M/100 EDTA standard solution is added to the sample solution by about two ml less than required volume, mix with stirring and, after adding in series triethanolamine, potassium hydroxide solution, and NN indicator, the titration is continued on to the end point.

11.2.5 Calculation The content percentage of the calcium oxide in the sample shall be calculated according to the following formula:

$$\text{CaO} = \frac{v \times f \times 0.0005608}{s} \times \frac{500}{25} \times 100$$

where CaO: content percentage of calcium oxide (%)

v : required volume of M/100 EDTA standard solution (ml)

f : factor of M/100 EDTA standard solution in 10.2.2 (8)

s : mass of sample weighed out in 11.2.3 (g)

11.3 Potassium Permanganate Titration Method

11.3.1 Summary Generate precipitate of calcium oxalate by adding ammonium oxalate into the sample solution (B) stored in 11.2.4 (2). After filtrating this precipitate, dissolve by using sulfuric acid, and titrate the isolated oxalic acid with potassium permanganate.

11.3.2 Reagent Reagents to be used shall be as follows:

- (1) Ammonium Oxalate Solution (4 W/V%)
- (2) Ammonium Acetate Solution (50 W/V%)
- (3) Sulfuric acid (1+4)

- (4) Potassium Permanganate Standard Solution Dissolve 2.26 g of potassium permanganate in water to dilute up to 1 l, and transfer it in a flask. After once boiling gently, let the solution stand in a dark place for one night, and filtrate the solution through a sintered glass filter G 4 (funnel type of Büchner funnel type) ⁽¹⁵⁾, store in a brown bottle. 1 ml of this solution is equivalent to about 0.002 g of calcium oxide.

Standardize this solution as follows.

Weigh out accurately 0.2 g of sodium oxalate ⁽¹⁶⁾ to the nearest 0.1 mg in a beaker (500 ml), and, after dissolving in 150 ml of warm water, add 50 ml of sulfuric acid (1+4). Heat the solution at about 70°C, and, while it is hot, titrate it with potassium permanganate standard solution. Make an end point when the faint pink colour of the solution lasts about 10 seconds. Calculate the quantity of calcium oxide equivalent to 1 ml of the standard solution according to the following formula, and round off the value to the fifth decimal place.

$$E = \frac{m \times 0.4185}{v}$$

where E : quantity of calcium oxide equivalent to 1 ml of potassium permanganate standard solution (g)

v : used volume of potassium permanganate standard solution (ml)

m : used quantity of sodium oxalate (g)

Notes ⁽¹⁵⁾ When the operation of boiling or filtrating is troublesome in such case as preparing a large amount of solution in one time, the following is preferable; after standing still the solution as it is for about one week, take supernatant aliquot from the solution by means of a syphon with a close attention lest the sedimentation deposited on a bottom should be disturbed.

⁽¹⁶⁾ Use the sodium oxalate specified in JIS K 8005, after heating at 150 to 200°C for 1 to 1.5 hours and cooling in a sulfuric acid desiccator.