

JIS

JAPANESE INDUSTRIAL STANDARD

**Chemical analysis of refractory
bricks and refractory mortars**

JIS R 2212^{—1991}

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In the event of any doubt arising,
the original Standard in Japanese is to be final authority.

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JAPANESE INDUSTRIAL STANDARD

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Chemical analysis of refractory bricks
and refractory mortars

R 2212-1991

1. Scope

This Japanese Industrial Standard specifies the chemical analysis of refractory bricks and refractory mortars.

Remarks: The following Standards are cited in this Standard:

JIS K 0050-General Rules for Chemical Analysis

JIS K 0115-General Rules for Molecular Absorptiometric Analysis

JIS K 0121-General Rules for Atomic Absorption Spectrochemical Analysis

JIS K 8001-General Rules of Testing Methods for Reagents

JIS K 8005-Standard Substances for Volumetric Analysis

JIS K 8885-Silicon Dioxide

JIS Z 8401-Rules for Rounding off of Numerical Values

JIS Z 8801-Test Sieves

2. General matters

General matters common to the chemical analysis shall be in accordance with JIS K 0050, JIS K 0115 and JIS K 0121. As for reagents, guaranteed grade reagents of JIS or those equal or superior thereto, shall be used.

3. Classes of chemical analysis of refractory bricks and refractory mortars

The chemical analysis of refractory bricks and refractory mortars shall be as follows:

- (1) Chemical analysis of fireclay brick and fireclay mortar
- (2) Chemical analysis of silica brick and silica refractory mortar
- (3) Chemical analysis of high-alumina refractory brick and high-alumina refractory mortar
- (4) Chemical analysis of magnesite brick and magnesite refractory mortar
- (5) Chemical analysis of magnesite-chrome brick and magnesite-chrome refractory mortar (containing chrome brick and chrome refractory mortar)

4. Sampling method

4.1 As for the analysis sample, grind all the test samples, pass them through 6.70 mm sieve of JIS Z 8801, take 100 g with a riffle sampler or by quartering and further grind all of them. Take 10 g from the sample totally passed through 300 μm sieve by quartering. Thinly spread the sample obtained by pulverizing more finely than the extent of totally passing through 90 μm sieve in a flat weighing bottle (50 mm in diameter) and dry it in an air bath at $110 \pm 5^\circ\text{C}$ for 2 h or more. Thereafter, reserve it in a desiccator. Take the sample therefrom.

4.2 In weighing out an analysis sample, weigh it out to the nearest 0.1 mg by using a chemical balance.

5. Rounding off of analysis value and tolerance

5.1 As a rule, analyze the same sample twice. When the difference thereof is larger than the numerical value given in the tolerance (%) of Table 1, analyze the sample again and allow average of numerical values obtained within the tolerance to be the analysis value.

Table 1. Tolerance of analysis value

Unit: %

Classes \ Item	Ig. loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	Cr ₂ O ₃
Fireclay brick and fireclay mortar	0.05	0.5	0.4	0.05	0.05	0.05	0.05	0.03	0.06	0.01	—
Silica brick and silica refractory mortar	0.05	0.5	0.1	0.05	0.05	0.10	0.05	0.01	0.02	0.01	—
High-alumina refractory brick and high-alumina refractory mortar (those of over 90 % in Al ₂ O ₃)	0.05	0.2	0.5	0.05	0.05	0.05	0.05	0.03	0.06	0.01	—
High-alumina refractory brick and high-alumina refractory mortar (those of under 90 % in Al ₂ O ₃)	0.05	0.5	0.5	0.05	0.05	0.05	0.05	0.03	0.06	0.01	—
Magnesite brick and magnesite refractory mortar	0.05	0.20	0.05	0.05	—	0.15	0.5	—	—	—	—
Magnesite-chrome brick and magnesite-chrome refractory mortar (containing chrome brick and chrome refractory mortar)	0.05	0.20	0.5	0.30	—	0.15	0.5	—	—	—	0.30

5.2 In analysis, carry out a blank test over all the operation and correct the content rate.

5.3 Express the analysis results by percentage and round off in accordance with JIS Z 8401 as follows:

- (1) The first decimal place in the case where the content rate is an integer of two figures.
- (2) The second decimal place in the case where the content rate is an integer of one figure.

A. Chemical analysis of fireclay brick and fireclay mortar1. Method for determination of ignition loss

1.1 Classification of methods The methods for determination of ignition loss shall be in accordance with gravimetric method.

1.2 Gravimetric method

1.2.1 Summary Measure the loss when a sample is ignited at about 1050°C to constant weight.

1.2.2 Weighing out amount of sample Weigh out 1 g of sample.

1.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample into a platinum crucible (for example, number 30) ⁽¹⁾, cover it with slightly leaving the clearance and ignite it at about 1050°C in an electric furnace for about 1 h. After standing it to cool in a desiccator, measure its mass.

Note ⁽¹⁾ A porcelain crucible (for example, PC 1 Type A 15 ml) may be used.

- (2) Repeat the operation for about 15 min each time and obtain the loss when the weight of sample has become constant.

1.2.4 Calculation Calculate the ignition loss of sample according to the following formula:

$$\text{Ignition loss (\%)} = \frac{w}{W} \times 100$$

where w : loss (g)

W : weighing out amount of sample (g)

2. Method for determination of silicon dioxide

2.1 Classification of methods The method for determination of silicon dioxide shall be in accordance with either one of the following methods:

- (1) Dehydration gravimetric absorptiometric combined method
- (2) Aggregation gravimetric absorptiometric combined method

2.2 Dehydration gravimetric absorptiometric combined method

2.2.1 Summary After fusing a sample with sodium carbonate, dissolve it with hydrochloric acid and evaporate it to dryness. After dehydrating silicic acid, dissolve the soluble salts with hydrochloric acid and filter it. Ignite the precipitate, measure it and add hydrofluoric acid. After evaporating silicon dioxide, ignite it, measure it again and obtain main silicon dioxide from its loss. Separately take the filtrate and obtain the amount of residual silicon dioxide by molybdenum blue absorptiometry. Allow the sum of both silicon dioxides to be total amount of silicon dioxide.

2.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1 + 1, 1 + 4, 1 + 50)
- (3) Potassium disulfate (Preliminarily fuse it, after cooling, grind it to be used.)
- (4) Hydrofluoric acid (46 %)
- (5) Hydrofluoric acid (1 + 9) Store the hydrofluoric acid (1 + 9) from which silicohydrofluoric acid is removed by adsorption by passing it through C1 type strong basic ion exchange column (Use the chromatotube made of plastics.), in a plastic bottle.
- (6) Sulfuric acid (1 + 1)
- (7) Boric acid (4 w/v %) Store it in a plastic bottle.
- (8) Sodium carbonate (anhydrous)
- (9) Ammonium molybdate solution Dissolve 10 g ammonium molybdate (4 hydrate) with water to 100 ml. If necessary, filter it and store it in a plastic bottle. However, when molybdic acid is deposited during storage, prepare it newly.
- (10) Tartaric acid solution Dissolve 10 g tartaric acid with water to 100 ml and store it in a plastic bottle.
- (11) Ascorbic acid solution (5 w/v %) Store said solution in a cool dark place. It should be preferable not to use the ascorbic acid solution for which one month or more has elapsed after preparation.
- (12) Standard silicon dioxide solution (0.05 mg SiO₂/ml) Ignite silicon dioxide of JIS K 8885 and let it stand to cool in a desiccator. Thereafter, weigh out 0.250 g into a platinum crucible and mix it with 1 g sodium carbonate (anhydrous). Thereafter, fuse it by heating. After standing to cool, dissolve it with water, transfer it into a one mark volumetric flask of 1000 ml, dilute it to the marked line with water and store it in a plastic bottle. Accurately dilute it five times with water at each service.

2.2.3 Weighing out amount of sample Weigh out 0.5 g of sample.

2.2.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample onto a platinum pan (for example, No. 75). After mixing it with 2 g sodium carbonate (anhydrous), at first heat it at a low temperature, gradually raise the temperature, lastly ignite it at about 1100°C in an electric furnace for about 10 min and fuse it.

- (2) After cooling, cover it with a watch glass, add 20 ml hydrochloric acid (1 + 1) and 1 ml sulfuric acid (1 + 1), dissolve it on a water bath by heating, wash the watch glass to be removed and successively evaporate it to dryness. At times, smash the deposited salts to powder with the glass rod the top of which is flattened during that time.
- (3) After standing to cool, add 5 ml hydrochloric acid, let it stand for about 1 min, add 20 ml hot water and dissolve the soluble salts by heating it on a water bath for about 5 min.
- (4) Add a suitable amount of powdery filter paper. After mixing them by stirring, filter it by using a filter paper (Class 5 B), wash it several times with hot hydrochloric acid (1 + 50) and further wash it with hot water until the reaction of chlorine ion disappears.

Receive the filtrate and washings in a beaker (300 ml) to be stored.
- (5) Put the precipitate together with the filter paper into a platinum crucible (for example, No. 30), add one drop sulfuric acid (1 + 1), at first heat it at a low temperature to incinerate the filter paper, and ignite at about 1100°C for about 1 h. After standing to cool in a desiccator, measure its mass and ignite it repeatedly to constant weight.
- (6) Moisten impure silicon dioxide with water, add 3 drops of sulfuric acid (1 + 1) and about 10 ml hydrofluoric acid and evaporate it to dryness by heating it on a sand bath. Ignite it at about 1100°C for about 5 min and let it stand to cool in a desiccator. Thereafter, measure its mass.
- (7) Fuse the residue in the crucible by adding about 1 g potassium disulfate thereto. After cooling, dissolve it with warm water and add it to the filtrate and washings of (4).
- (8) Transfer the solution of (4) into a one mark volumetric flask of 250 ml (2) and dilute it up to the marked line with water to be stored. Allow this solution to be the sample solution (A) and use it for determination of residual silicon dioxide, aluminium oxide, ferric oxide, and titanium dioxide.
- (9) Accurately, separately take 10 ml from this sample solution (A) into a plastic beaker (100 ml).
- (10) Add 2 ml hydrofluoric acid (1 + 9) and let it stand for about 10 min. Thereafter, add 50 ml boric acid solution and dilute it to about 70 ml with water.
- (11) Add 2 ml ammonium molybdate solution, mix them by shaking and let it stand for 10 min. After adding 5 ml tartaric acid solution, add 2 ml ascorbic acid solution, transfer it into a one mark volumetric flask of 100 ml, dilute it up to the marked line with water and let it stand for 30 min.

- (12) Take a portion of this solution into the absorption cell of a photometer and measure the absorbance at nearly 650 nm in wavelength.

Note (2) When the amount of reserved solution is much, concentrate it on a sand bath and put it into a one mark volumetric flask of 250 ml.

2.2.5 Calculation Obtain the amount of residual silicon dioxide from the working curve prepared in 2.2.6 and calculate the content rate of silicon dioxide in sample according to the following formula:

$$\text{Silicon dioxide (\%)} = \frac{(w_1 - w_2) + a \times \frac{250}{10}}{W} \times 100$$

where, w_1 : mass measured in 2.2.4 (5) (g)

w_2 : mass measured in 2.2.4 (6) (g)

a : detection amount of residual silicon dioxide in 2.2.4 (12) (g)

W : weighing out amount of sample (g)

2.2.6 Preparation of working curve Stepwise take 0 to 6.0 ml standard silicon dioxide solution (0 to 0.3 mg as silicon dioxide) into a plastic beaker (100 ml), add 1 ml hydrochloric acid (1 + 4) to each of them, thereafter operate it in accordance with the procedures of 2.2.4 (10) to (12) and prepare the relation curve between the obtained absorbance and the amount of silicon dioxide to be the working curve.

2.3 Aggregation gravimetric absorptiometric combined method

2.3.1 Summary After fusing a sample with sodium carbonate and boric acid, dissolve it with hydrochloric acid and aggregate silicic acid by adding polyethylene oxide. Thereafter, filter it. Ignite the precipitate, measure it and add hydrofluoric acid. After evaporating silicon dioxide, ignite it again, measure it and obtain the amount of main silicon dioxide from the loss thereof. Separately take the filtrate and obtain the amount of residual silicon dioxide by molybdenum blue absorptiometry. Allow the sum of both amounts to be the total amount of silicon dioxide.

2.3.2 Reagents The reagents shall be as follows:

- (1) Boric acid
- (2) Polyethylene oxide solution Add little by little 0.1 g polyethylene oxide to 200 ml water while mixing them by stirring to be dissolved and store it in a plastic bottle. It should be preferable not to use the polyethylene oxide solution for which two weeks have elapsed after preparation.
- (3) As for other reagents, use the same ones as the reagents of 2.2.2 (2) to (12).

2.3.3 Weighing out amount of sample Weigh out 0.5 g of sample.

2.3.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample onto a platinum pan (for example, No. 75), add 2 g sodium carbonate (anhydrous) and 0.3 g boric acid and mix them. Thereafter, at first heat it at a low temperature, gradually raise the temperature, ignite it at about 1000°C for about 10 min and fuse it ⁽³⁾.
- (2) Cover it with a watch glass. After standing to cool, add 20 ml hydrochloric acid (1 + 1) and dissolve it by heating on a water bath. Thereafter, continue to heat it as it is for about 20 min.
- (3) Remove the watch glass without washing it with water ⁽⁴⁾, add a suitable amount of powdery filter paper and mix them by stirring. Thereafter, add about 10 ml polyethylene oxide solution, sufficiently mix them by stirring and let it stand as it is for about 5 min.
- (4) Filter it by using a filter paper (Class 5 B), wash it several times with hot hydrochloric acid (1 + 50) and further wash it with hot water until the reaction of chlorine ion disappears. Receive the filtrate and washings with a beaker (300 ml) and reserve.
- (5) Put the precipitate together with the filter paper into a platinum crucible (for example, No. 30), add one drop sulfuric acid (1 + 1), at first heat it at a low temperature to incinerate the filter paper and ignite it at about 1100°C for about 1 h. After standing to cool in a desiccator, measure the mass and ignite it repeatedly to constant weight.
- (6) Moisten impure silicon dioxide with water, add three drops of sulfuric acid (1 + 1) and about 10 ml hydrofluoric acid and evaporate it to dryness by heating on a sand bath. Ignite it at about 1100°C for about 5 min and let it stand to cool in a desiccator. Thereafter, measure the mass.
- (7) Fuse the residue in the crucible by adding about 1 g potassium disulfate thereto. After cooling, dissolve it with warm water and add it to the filtrate and washings of (4).
- (8) Transfer the solution of (4) into a one mark volumetric flask of 250 ml ⁽²⁾ and dilute it up to the marked line with water to be stored. Allow this solution to be the sample solution (A) and use it for determination of residual silicon disulfate, aluminium oxide, ferric oxide, and titanium dioxide.
- (9) Hereafter, operate it in accordance with the procedures of 2.2.4 (9) to (12).

Notes ⁽³⁾ If the fusing time is excessively long, the sample becomes difficult to be dissolved with hydrochloric acid.

⁽⁴⁾ Carry out the washing of watch glass at the time of the operation of (4).

2.3.5 Calculation Obtain the amount of residual silicon dioxide from the working curve prepared in 2.3.6 and calculate the content rate of silicon dioxide in sample according to the following formula:

$$\text{Silicon dioxide (\%)} = \frac{(w_1 - w_2) + a \times \frac{250}{10}}{W} \times 100$$

where, w_1 : mass measured in 2.3.4 (5) (g)

w_2 : mass measured in 2.3.4 (6) (g)

a : detection amount of residual silicon dioxide in 2.3.4 (9) (g)

W : weighing out amount of sample (g)

2.3.6 Preparation of working curve Carry out the operation in the same way as in 2.2.6.

3. Method for determination of aluminium oxide

3.1 Classification of method The method for determination of aluminium oxide shall be as described in EDTA-zinc back-titrimetric method.

3.2 EDTA-zinc back-titrimetric method

3.2.1 Summary Separately take the sample solution (A), regulate pH at 5.5 by adding excess EDTA and complete aluminium-EDTA chelate by boiling. After cooling, utilize Xylenol Orange as indicator and back-titrate it with zinc standard solution.

3.2.2 Reagents The reagents shall be as follows:

- (1) Aqueous ammonia (1 + 9)
- (2) Buffer solution (5.5 in pH) Dissolve 250 g sodium acetate (3 hydrate) with about 1 l water and regulate pH at 5.5 by adding acetic acid.
- (3) EDTA solution (0.02 M) Dissolve 7.5 g disodium ethylenediaminetetraacetate (2 hydrate) with water to 1000 ml. Reserve it in a plastic bottle.
- (4) M/50 zinc standard solution Accurately weigh out 1.31 g zinc of JIS K 8005 into a beaker (300 ml) to the nearest 0.1 mg, add about 10 ml water and 10 ml nitric acid (1 + 1), cover it with a watch glass and dissolve it by heating on a water bath. Wash the watch glass with water to be removed and regulate pH at 5.5 by adding about 100 ml water and ammonium acetate solution (10 w/v %). Thereafter, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Store it in a plastic bottle.

Calculate the aluminium oxide amount (g) equivalent to 1 ml of this solution according to the following formula:

$$f = \frac{G \times P}{1.3074 \times 100} \times 0.0010196$$

where, f : aluminium oxide amount equivalent to 1 ml M/50 zinc standard solution (g)

G : weighing out amount of zinc (g)

P : purity of zinc (%)

- (5) Xylenol Orange solution (0.1 w/v %) Dissolve 0.1 g 3, 3'-bis [N, N-di (carboxymethyl)-aminomethyl] -o- cresolsulphophthalein with 100 ml water, put it into a brown bottle and store it in a cool, dark place. Prepare it at each 1 to 2 months.
- (6) Methyl Orange solution (0.1 w/v %)

3.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Accurately, separately take 50 ml from the sample solution (A) reserved in 2.2.4 (8) or 2.3.4 (8) into a beaker (300 ml), accurately add a specified amount ⁽⁵⁾ of EDTA solution and add about 100 ml hot water. Thereafter, add one drop Methyl Orange solution as indicator and drop aqueous ammonia (1 + 9) while stirring them until the color of solution turns to orange. Then, add 10 ml buffer solution (5.5 in pH) and boil it for about 5 min.
- (2) After cooling, add 4 to 5 drops Xylenol Orange solution as indicator and titrate it with M/50 zinc standard solution until the solution turns reddish.

Note ⁽⁵⁾ The additional amount of EDTA solution shall be as given in Table 2 according to the content rate of aluminium oxide in sample.

Table 2. Additional amount of EDTA solution

Content rate of aluminium oxide %	Additional amount ml
Under 30	40
30 or over to and excl. 35	45
35 or over to and excl. 40	50
40 or over to and excl. 45	55

3.2.4 Blank test Accurately, separately take 50 ml from the solution of blank test reserved in 2.2.4 (8) or in 2.3.4 (8) by using only reagents, carry out the operation on and after the accurate addition of a specified amount of EDTA solution of 3.2.3 (1) and titrate it with M/50 zinc standard solution until the solution turns reddish.

3.2.5 Calculation Calculate the content rate of aluminium oxide in sample according to the following formula:

$$\text{Aluminium oxide (\%)} = \frac{(V_1 - V_2) \times f}{W} \times \frac{250}{50} \times 100 - (\text{Fe}_2\text{O}_3 + \text{TiO}_2) \times 0.638$$

where, V_1 : used amount of M/50 zinc standard solution in 3.2.4 (ml)

V_2 : used amount of M/50 zinc standard solution in 3.2.3 (2) (ml)

f : aluminium oxide amount equivalent to 1 ml M/50 zinc standard solution (g)

W : weighing out amount of sample in 2.2.3 or in 2.3.3 (g)

Fe_2O_3 : ferric oxide content rate obtained in 4.2 (%)

TiO_2 : titanium dioxide content rate obtained in 5.2 or in 5.3 (%)

Remarks: When the content of manganese monoxide in a test sample is much, sodium fluoride addition EDTA-zinc back-titrimetric method shall be applied.

(1) Sodium fluoride addition EDTA-zinc back-titrimetric method

(a) Add 1.0 g sodium fluoride to the solution titrated in 3.2.3 (2) and boil it for 5 min by heating. After cooling, titrate it again with M/50 zinc standard solution until the solution turns slightly reddish.

(b) **Calculation** Calculate the content rate of aluminium oxide in sample according to the following formula:

$$\text{Aluminium oxide (\%)} = \frac{V \times f}{W} \times \frac{250}{50} \times 100 - \text{TiO}_2 \times 0.638$$

where, V : used amount of M/50 zinc standard solution (ml)

f : aluminium oxide amount equivalent to 1 ml M/50 zinc standard solution (g)

W : weighing out amount of sample (g)

TiO_2 : titanium dioxide content rate obtained in 5.2 or in 5.3 (%)

4. Method for determination of ferric oxide

4.1 Classification of method The method for determination of ferric oxide shall be in accordance with 1, 10-phenanthroline absorptiometry.

4.2 1, 10-Phenanthroline absorptiometry

4.2.1 Summary Separately take the sample solution (A), reduce iron with hydroxylamine hydrochloride, add 1, 10-phenanthroline, color it by regulating pH with buffer solution and measure the absorbance.

4.2.2 Reagents The reagents shall be as follows:

- (1) Hydroxylamine hydrochloride solution (10 w/v %)
- (2) 1, 10-Phenanthroline solution Dissolve 0.12 g 1, 10-phenanthroline hydrochloride (monohydrate) with water to 100 ml. Reserve it in a cool, dark place. However, when colored during storage, prepare it newly.
- (3) Buffer solution Dissolve 200 g ammonium acetate with water to 1 l.
- (4) Standard ferric oxide solution (0.02 mg $\text{Fe}_2\text{O}_3/\text{ml}$) Weigh out 0.140 g pure iron (99.9 % min.) into a beaker (300 ml), add 20 ml hydrochloric acid (1 + 1), decompose it by heating and carefully drop 1 ml hydrogen peroxide water thereto. Thereafter, oxidize iron by boiling and further, continue to boil it. After decomposing excess hydrogen peroxide water, cool it, transfer it into a one mark volumetric flask of 1000 ml and accurately dilute it up to the marked line with water. Accurately dilute it 10 times at each service.

4.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Accurately, separately take a specified amount ⁽⁶⁾ from the sample solution (A) reserved in 2.2.4 (8) or in 2.3.4 (8) into a one mark volumetric flask of 100 ml.
- (2) Dilute it to about 60 ml with water, add 2 ml hydroxylamine hydrochloride solution, mix them by shaking, add 10 ml 1, 10-phenanthroline solution and 10 ml buffer solution, add water up to the marked line, mix them by shaking and let it stand as it is for 30 min.
- (3) Take a portion of this solution into the absorption cell of a photometer and measure the absorbance at nearly 510 nm in wavelength.

Note ⁽⁶⁾ The aliquot amount of sample solution (A) shall be as given in Table 3 according to the content rate of ferric oxide in sample.

Table 3. Aliquot amount of sample solution (A)

Content rate of ferric oxide %	Aliquot amount ml
Under 0.5	25
0.5 or over to and excl. 1.5	10
1.5 or over	5

4.2.4 Calculation Obtain the amount of ferric oxide from the working curve prepared in 4.2.5 and calculate the content rate of ferric oxide in sample according to the following formula:

$$\text{Ferric oxide (\%)} = \frac{a}{w} \times \frac{250}{V} \times 100$$

where, a : detection amount of ferric oxide in 4.2.3 (3) (g)

w : weighing out amount of sample in 2.2.3 or in 2.3.3 (g)

v : aliquot amount of sample solution (A) (ml)

4.2.5 preparation of working curve Stepwise take 0 to 20 ml standard ferric oxide solution (0 to 0.4 mg as ferric oxide) into a one mark volumetric flask of 100 ml, operate it in accordance with the procedures of 4.2.3 (2) to 4.2.3 (3) and prepare the relation curve between the obtained absorbance and the amount of ferric oxide to be the working curve.

5. Method for determination of titanium dioxide

5.1 Classification of methods The method for determination of titanium dioxide shall be in accordance with either one of the following methods.

- (1) Diantipyrylmethane absorptiometry This method is not applicable to the sample of not less than 1 % in titanium dioxide.
- (2) Hydrogen peroxide absorptiometry This method is applied to the sample of not less than 0.5 % in titanium dioxide.

5.2 Diantipyrylmethane absorptiometry

5.2.1 Summary Separately take the sample solution (A). After regulating the concentration of hydrochloric acid, reduce iron by adding ascorbic acid, color it with diantipyrylmethane and measure the absorbance.

5.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1)
- (2) Ascorbic acid solution (5 w/v %) Reserve the ascorbic acid solution in a cool, dark place. It should be preferable not to use the ascorbic acid solution for which one month or more has elapsed after preparation.

- (3) Diantipyrylmethane solution Dissolve 1 g diantipyrylmethane with 30 ml hydrochloric acid (1 + 5) and dilute it with water to 100 ml.
- (4) Standard titanium dioxide solution (0.2 mg TiO₂/ml) Take titanium dioxide (99.9 % min.) into a crucible, ignite it at about 1100°C for about 1 h and let it stand to cool in a desiccator. Weigh out 0.200 g therefrom into a platinum crucible and fuse it by adding 4 g potassium disulfate. After standing to cool, put the platinum crucible into a beaker, add hydrochloric acid (1 + 9) and fuse it at 50°C max. by heating. After cooling, take out the platinum crucible and wash it with water. Thereafter, transfer the solution into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with hydrochloric acid (1 + 9).

5.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Accurately, separately take a specified amount ⁽⁷⁾ from the sample solution (A) reserved in 2.2.4 (8) or in 2.3.4 (8) into a one mark volumetric flask of 50 ml.
- (2) Add 5 ml hydrochloric acid (1 + 1) and 2 ml ascorbic acid solution. After standing as it is for 1 min, add 15 ml diantipyrylmethane solution, dilute it up to the marked line with water and let it stand as it is for 1 h.
- (3) Take a portion of this solution into the absorption cell of a photometer and measure the absorbance at nearly 390 nm in wavelength.

Note ⁽⁷⁾ The aliquot amount of sample solution shall be as given in Table 4 according to the content rate of titanium in sample.

Table 4. Aliquot amount of sample solution (A)

Content rate of titanium dioxide %	Aliquot amount ml
Under 0.30	25
0.30 or over to and excl. 0.80	10
0.80 or over	5

5.2.4 Calculation Obtain the amount of titanium dioxide from the working curve prepared in 5.2.5 and calculate the content rate of titanium dioxide in sample according to the following formula:

$$\text{Titanium dioxide (\%)} = \frac{a}{W} \times \frac{250}{V} \times 100$$

where, a : detection amount of titanium dioxide in 5.2.3 (3) (g)

W : weighing out amount of sample in 2.2.3 or in 2.3.3 (g)

V : aliquot amount of sample solution (A) (ml)

5.2.5 Preparation of working curve Accurately dilute standard titanium dioxide solution 20 times with water, stepwise take 0 to 25 ml (0 to 0.25 mg as titanium dioxide) into a one mark volumetric flask of 50 ml, operate it in accordance with the procedures on and after the addition of hydrochloric acid (1 + 1) of 5.2.3 (2) and prepare the relation curve between the obtained absorbance and the amount of titanium dioxide to prepare the working curve.

5.3 Hydrogen peroxide absorptiometry

5.3.1 Summary Separately take the sample solution (A). After masking iron by adding phosphoric acid, color it with hydrogen peroxide water and measure the absorbance.

5.3.2 Reagents The reagents shall be as follows:

- (1) Phosphoric acid (1 + 1)
- (2) Hydrogen peroxide water (1 + 9)
- (3) Standard titanium dioxide solution Use the same solution as standard titanium dioxide solution in 5.2.2 (4).

5.3.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Accurately, separately take 25 ml from the sample solution (A) reserved in 2.2.4 (8) or in 2.3.4 (8) into a one mark volumetric flask of 50 ml.
- (2) Add 5 ml phosphoric acid (1 + 1) and 5 ml hydrogen peroxide water (1 + 9) and dilute it up to the marked line with water.
- (3) Take a portion of this solution into the absorption cell of a photometer, accurately, separately take 25 ml from the sample solution (A) reserved in 2.2.4 (8) or in 2.3.4 (8) into a one mark volumetric flask of 50 ml, add 5 ml phosphoric acid (1 + 1), dilute it up to the marked line with water, utilize this diluted solution as contrast solution and measure the absorbance at nearly 410 nm in wavelength.

5.3.4 Calculation Obtain the amount of titanium dioxide from the working curve prepared in 5.3.5 and calculate the content rate of titanium dioxide in sample according to the following formula:

$$\text{Titanium dioxide (\%)} = \frac{a}{W} \times \frac{250}{25} \times 100$$

where, a : detection amount of titanium dioxide in 5.3.3 (3) (g)

W : weighing out amount of sample in 2.2.3 or in 2.3.3 (g)

5.3.5 Preparation of working curve Stepwise take 0 to 10.0 ml standard titanium dioxide solution (0 to 20.0 mg as titanium dioxide) into a one mark volumetric flask of 50 ml, add 5 ml phosphoric acid (1 + 1) and 5 ml hydrogen peroxide water (1 + 9) and dilute it up to the marked line with hydrochloric acid (1 + 9). Take a portion of this solution into the absorption cell of a photometer and measure the absorbance at nearly 410 nm in wavelength. Prepare the relation curve between the obtained absorbance and the amount of titanium dioxide to be the working curve.

6. Method for determination of calcium oxide

6.1 Classification of methods The method for determination of calcium oxide shall be in accordance with either one of the following methods.

- (1) EDTA titrimetric method
- (2) Atomic absorption method

6.2 EDTA titrimetric method

6.2.1 Summary Decompose a sample with hydrofluoric acid and sulfuric acid and evaporate it to dryness. Thereafter, dissolve it with hydrochloric acid to constant volume. Separately take a portion thereof, add triethanolamine and potassium cyanide, mask interfering ions and regulate pH at about 13 by adding potassium hydroxide. Thereafter, utilize calcein as indicator and titrate the solution with EDTA standard solution.

6.2.2 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) Potassium hydroxide solution Dissolve 250 g potassium hydroxide with water to 1 l. Reserve it in a plastic bottle.
- (6) Potassium cyanide solution (10 w/v %) Reserve the potassium cyanide solution in a plastic bottle.
- (7) Triethanolamine (1 + 2)
- (8) M/100 EDTA standard solution Weigh out 3.75 g disodium ethylenediaminetetraacetate (2 hydrate) into a beaker (300 ml), dissolve it with about 100 ml water and dilute it with water to 1000 ml. Reserve it in a plastic bottle. Allow the standardization of this solution shall be in accordance with 4.4 of JIS K 8001.
- (9) Calcein indicator Grind 0.1 g fluoresceine bismethylimine diacetate and 10 g potassium sulfate to be mixed.

6.2.3 Weighing out amount of sample Weigh out 0.5 g of sample.

6.2.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out a sample onto a platinum pan (for example No. 75), moisten it with water, add 3 ml sulfuric acid (1 + 1), 2 ml nitric acid, and 10 ml hydrofluoric acid, sufficiently mix them by stirring with platinum wire, carefully decompose it by heating on a sand bath, violently generate white fume of sulfuric acid and evaporate it to dryness.
- (2) After standing to cool, wash the inside wall of platinum pan with water, add 1 ml sulfuric acid (1 + 1) and evaporate it to dryness again by heating.
- (3) After standing to cool, add 5 ml hydrochloric acid (1 + 1) and about 10 ml water, cover it with a watch glass and heat it on a water bath for about 10 min.
- (4) After cooling, wash the watch glass with water to be removed⁽⁸⁾, transfer it into a one mark volumetric flask of 250 ml and dilute it up to the marked line.

Allow this solution to be the sample solution (B) and utilize it for determination of calcium oxide and magnesium oxide by EDTA titrimetric method and of sodium oxide and potassium oxide by flame method.

- (5) Accurately, separately take 100 ml from sample solution (B) into a beaker (500 ml), dilute it to about 200 ml with water, add 20 ml triethanolamine (1 + 2), about 10 ml potassium hydroxide solution, and 1 ml potassium cyanide solution and let them stand as it is for several minutes.
- (6) Add about 0.05 g calcein indicator and titrate the solution with M/100 EDTA standard solution until fluorescent green disappears and the solution turns orange⁽⁹⁾ ⁽¹⁰⁾.

Notes ⁽⁸⁾ When insoluble residue is observed, filter it with a filter paper (Class 5 B).

⁽⁹⁾ If the titration is carried out on a black paper or a black plate, the end point is easy to be decided.

⁽¹⁰⁾ As for the solution after titration, discard it after the treatment of decomposition of cyan ion.

6.2.5 Calculation Calculate the content rate of calcium oxide in sample according to the following formula:

$$\text{Calcium oxide (\%)} = \frac{V_1 \times f \times 0.005608}{W} \times \frac{250}{100} \times 100$$

where, V_1 : used amount of M/100 EDTA standard solution in 6.2.4 (6) (ml)

f : factor of M/100 EDTA standard solution

W : weighing out amount of sample in 6.2.3 (g)

6.3 Atomic absorption method

6.3.1 Summary Decompose a sample with hydrofluoric acid and perchloric acid. After evaporating it to dryness, dissolve it with hydrochloric acid and add lanthanum chloride to it to constant volume. Take a portion of this solution and measure the absorbance of calcium by using an atomic absorption analyzer.

6.3.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1)
- (2) Nitric acid
- (3) Perchloric acid (60 to 70 %)
- (4) Hydrofluoric acid (46 %)
- (5) Lanthanum chloride solution (1¹) Add 200 ml hydrochloric acid (1 + 1) to 50 g lanthanum oxide, dissolve it by heating and dilute it with water to 1 l. Reserve it in a plastic bottle.
- (6) Aluminium chloride solution Weigh out 1.75 g metallic aluminium (99.9 % min.), add 50 ml hydrochloric acid (1 + 1) and dissolve it by heating. After cooling, transfer it into a one mark volumetric flask of 500 ml and dilute it up to the marked line with water. Allow 1 ml this solution to be equivalent to 6.6 mg aluminium oxide. Reserve it in a plastic bottle.
- (7) Standard calcium oxide solution (0.5 mg CaO/ml) Weigh out 0.892 g calcium carbonate and dissolve it with gradually adding 30 ml hydrochloric acid (1 + 1). After cooling, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Reserve it in a plastic bottle.
- (8) Standard magnesium oxide solution (0.1 mg MgO/ml) Weigh out 0.603 g metallic magnesium (99.9 % min.), gradually add 30 ml hydrochloric acid (1 + 1) and dissolve it by heating. After cooling, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Accurately dilute it 10 times to be used. Reserve it in a plastic bottle.
- (9) Standard sodium oxide solution (0.5 mg Na₂O/ml) Dissolve 0.943 g sodium chloride in water, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Reserve it in a plastic bottle.
- (10) Standard potassium oxide solution (0.5 mg K₂O/ml) Dissolve 0.792 g potassium chloride in water, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Reserve it in a plastic bottle.

- (11) **Standard mixed solution series-1** Stepwise take respective standard solutions of calcium oxide, magnesium oxide, sodium oxide, and potassium oxide into one mark volumetric flasks of 100 ml ⁽¹²⁾, add 10 ml aluminium chloride solution, 10 ml lanthanum chloride solution, and 4 ml hydrochloric acid (1 + 1) to each of them and dilute them up to the marked line with water. Reserve them in a plastic bottles.

Notes ⁽¹¹⁾ Strontium chloride solution may be used. In that case, 122 g strontium chloride (6 hydrate) is dissolved in water, joined by 40 ml hydrochloric acid (1 + 1) and diluted to 1 l with water. It is reserved in a plastic bottle.

- ⁽¹²⁾ The aliquot amount of each standard solution should preferably be of concentration equivalent to the content range of each component contained in the sample. Examples are given in Table 5.

Table 5. Example of standard mixed solution series-1

Standard mixed solution Series-1	Aluminium chloride solution additional amount ml	Lanthanum chloride solution additional amount ml	Hydrochloric acid (1+1) additional amount ml	Calcium oxide solution		Magnesium oxide solution		Sodium oxide solution		Potassium oxide solution	
				Standard solution additional amount ml	Concentration mg/100 ml	Standard solution additional amount ml	Concentration mg/100 ml	Standard solution additional amount ml	Concentration mg/100 ml	Standard solution additional amount ml	Concentration mg/100 ml
1	10	10	4	0	0	0	0	0	0	0	0
2	10	10	4	1.0	0.5	1.0	0.1	1.0	0.5	1.0	0.5
3	10	10	4	2.0	1.0	2.0	0.2	2.0	1.0	2.0	1.0
4	10	10	4	3.0	1.5	3.0	0.3	3.0	1.5	3.0	1.5
5	10	10	4	4.0	2.0	4.0	0.4	4.0	2.0	4.0	2.0
6	10	10	4	5.0	2.5	5.0	0.5	5.0	2.5	5.0	2.5
7	10	10	4	6.0	3.0	6.0	0.6	6.0	3.0	6.0	3.0
8	10	10	4	7.0	3.5	7.0	0.7	7.0	3.5	7.0	3.5
9	10	10	4	8.0	4.0	8.0	0.8	8.0	4.0	8.0	4.0
10	10	10	4	9.0	4.5	9.0	0.9	9.0	4.5	9.0	4.5

6.3.3 **Apparatus** Use an atomic absorption analyzer.

6.3.4 **Weighing out amount of sample** Weigh out 0.2 g of sample.

6.3.5 **Operation** Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample onto a platinum pan (for example, No. 75), moisten it with water, add 5 ml perchloric acid, 2 ml nitric acid, and 10 ml hydrofluoric acid, sufficiently mix them by stirring with platinum wire, carefully decompose it by heating on a sand bath, violently generate white fume of perchloric acid and evaporate it to dryness.
- (2) After standing to cool, wash the inside wall of platinum pan with water, add 3 ml perchloric acid and violently generate white fume by heating again. When the sample becomes near dryness, thoroughly dry it up at a slightly lower temperature.
- (3) Add 5 ml hydrochloric acid (1 + 1) and about 10 ml water, cover it with a watch glass and heat it on a water bath for about 10 min.
- (4) After cooling, wash the watch glass with water to be removed, transfer it into a one mark volumetric flask of 100 ml ⁽⁸⁾, add 10 ml lanthanum chloride solution and dilute it up to the marked line with water. Allow this solution to be the sample solution (C) and utilize it for determination of calcium oxide, magnesium oxide, sodium oxide, and potassium oxide according to atomic absorption method.
- (5) Take a portion of this sample solution (C), use the light source lamp for calcium of atomic absorption analyzer and measure the absorbance at 422.7 nm in wavelength ⁽¹³⁾.

Note ⁽¹³⁾ As for lamp current value, slit width of spectroscope, the pressure and flow rate of combustible gas and ignition improver gas, the position of luminous flux transmitted through the flame, suitable conditions are established according to each apparatus. When the sensitivity is insufficient, it is regulated by using a scale magnifying device, or otherwise with the sensitivity regulator built in the apparatus.

Further, when the sensitivity is high, the measuring sensitivity is reduced by regulation of luminous flux angle or the like.

6.3.6 Calculation Obtain the concentration of calcium oxide from the working curve prepared in 6.3.7 and calculate the content rate of calcium oxide in sample according to the following formula:

$$\text{Calcium oxide (\%)} = \frac{C \times 10^{-3}}{W} \times 100$$

where, C: concentration of calcium oxide in sample solution (C) (mg/100 ml)

W: weighing out amount of sample in 6.3.4 (g)

6.3.7 Preparation of working curve Utilize the light source lamp for calcium, respectively measure the absorbances at 422.7 nm in wavelength of standard mixed solution series-1 and prepare the relation curve between the obtained absorbances and the concentrations of calcium oxide to be the working curve.

7. Method for determination of magnesium oxide

7.1 Classification of methods The method for determination of magnesium oxide shall be in accordance with either one of the following methods.

- (1) EDTA titrimetric method
- (2) Atomic absorption method

7.2 EDTA titrimetric method

7.2.1 Summary Separately take the sample solution (B), add ammonium tartrate, triethanolamine, and potassium cyanide, mask the interfering ions and regulate pH at about 10 by adding aqueous ammonia. Utilize methyl red and methylthymol blue as indicator and titrate the total amount of calcium oxide and magnesium oxide with EDTA standard solution. Obtain magnesium oxide by subtracting the calcium oxide titrated in 6.2 therefrom.

7.2.2 Reagents The reagents shall be as follows:

- (1) Aqueous ammonia (1 + 1)
- (2) Ammonium tartrate solution (10 w/v %)
- (3) Methyl red solution Dissolve 0.1 g methyl red with 100 ml ethanol (95 w/v %).
- (4) Methylthymol blue indicator Grind 0.1 g 3,3'-bis [N, N-di (carboxymethyl)-aminomethyl] thymolsulphophthalein (sodium salt) with 10 g potassium sulfate to be mixed.
- (5) As for other reagents, use the same reagents as (6) to (8) of 6.2.2.

7.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Accurately, separately take 100 ml from the sample solution (B) obtained in 6.2.4 (4) into a beaker (500 ml) and add 5 ml ammonium tartrate solution, 60 ml triethanolamine (1 + 2), 35 ml aqueous ammonia (1 + 1), and 1 ml potassium cyanide solution.
- (2) Add one drop methyl red solution and about 0.05 g methylthymol blue indicator and titrate the solution with M/100 EDTA standard solution until the blue disappears and the color turns to faint yellow.

7.2.4 Calculation Calculate the content rate of magnesium oxide in sample according to the following formula:

$$\text{Magnesium oxide (\%)} = \frac{(V_2 - V_1) \times f \times 0.0004032}{W} \times \frac{250}{100} \times 100$$

where, f : factor of M/100 EDTA standard solution

V_1 : used amount of M/100 EDTA standard solution
in 6.2.4 (6) (ml)

V : used amount of M/100 EDTA standard solution in 7.2.3 (2) (ml)

W : weighing out amount of sample in 6.2.3 (g)

7.3 Atomic absorption method

7.3.1 Summary Separately take the sample solution (C) and dilute it with dilute hydrochloric acid to constant volume. Take a portion of this solution, utilize an atomic absorption analyzer and measure the absorbance of magnesium.

7.3.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 39)
- (2) Standard mixed solution series-1 Use the same standard mixed solution series-1 as in 6.3.2 (11).

7.3.3 Apparatus Use an atomic absorption analyzer.

7.3.4 Operation As for the determination operation, separately take a specified amount of sample solution (C) obtained in 6.3.5 (4) and accurately dilute it with hydrochloric acid (1 + 39) to 100 ml (for example 10 times) to be the sample solution (D). Take a portion of this solution, utilize the light source lamp for magnesium of atomic absorption analyzer and measure the absorbance at 285.2 nm in wavelength (¹³).

7.3.5 Calculation Obtain the concentration of magnesium oxide from the working curve prepared in 7.3.6 and calculate the content rate of magnesium oxide in sample from the following formula:

$$\text{Magnesium oxide (\%)} = \frac{C \times 10^{-3}}{W} \times \frac{100}{V} \times 100$$

where, C : concentration of magnesium oxide in sample solution (D) (mg/100 ml)

W : weighing out amount of sample in 6.3.4 (g)

V : aliquot amount of sample solution (C) (ml)

7.3.6 Preparation of working curve Accurately dilute standard mixed solution series-1 of 6.3.2 (11) with hydrochloric acid (1 + 39) by the same proportion as that of sample solution of 7.3.4 (for example, ten times), utilize the light source lamp for magnesium, respectively measure the absorbances at 285.2 nm in wavelength of dilute standard solution series and prepare the relation curve between the obtained absorbances and the concentrations of magnesium oxide to be the working curve.

8. Method for determination of sodium oxide

8.1 Classification of methods The method for determination of sodium oxide shall be in accordance with either one of the following methods:

- (1) Flame method
- (2) Atomic absorption method

8.2 Flame method

8.2.1 Summary Take a portion of sample solution (B) and measure the emission line intensity of sodium by utilizing a flame photometer.

8.2.2 Reagents The reagents shall be as follows:

- (1) Aluminium chloride solution Use the same solution as in 6.3.2 (6).
- (2) Standard sodium oxide solution (0.25 mg Na₂O/ml) Dilute the solution of 6.3.2 (9) two times to be used.
- (3) Standard potassium oxide solution (0.5 mg K₂O/ml) Use the same solution as in 6.3.2 (10).
- (4) Standard mixed solution series-2 Stepwise take respective standard solutions of sodium oxide and potassium oxide into one mark volumetric flasks of 100 ml ⁽¹⁴⁾, add 10 ml aluminium chloride solution and 2 ml hydrochloric acid (1 + 1) to each of them and dilute them up to the marked line with water. Reserve them in a plastic bottles.

Note ⁽¹⁴⁾ The aliquot amount of standard alkali stock solution should preferably be of concentration equivalent to the content rate range of each component contained in the sample. Examples are given in Table 6.

8.2.3 Apparatus Use a flame photometer.

8.2.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Regulate the measuring wavelength of flame photometer at 589 nm ⁽¹⁵⁾.
- (2) Spray the solution of a suitable concentration ⁽¹⁶⁾ among standard mixed solution series-2 and regulate the operation so that the pointer of meter indicates a specified value (for example, 100) ⁽¹⁷⁾. Then, spray water and regulate the operation so that the pointer of meter indicates zero. Alternately repeat those operations and regulate the operation until the pointer of meter indicates accurately a specified value ⁽¹⁷⁾ and zero respectively with the solution of concentration ⁽¹⁶⁾ among standard mixed solution series-2 and water.
- (3) Spray a portion of sample solution (B) obtained in 6.2.4 (4) and read out the meter ⁽¹⁸⁾.

Notes ⁽¹⁵⁾ The filter for sodium may be used.

⁽¹⁶⁾ The solution among standard mixed solution series-2 of slightly higher concentration than that of sample solution (B), shall be used.

⁽¹⁷⁾ This specified value should preferably be not less than 80.

- (¹⁸) Each time confirm that the pointer of meter indicates a specified value (¹⁷) and zero by using the solution of a suitable concentration (¹⁶) in standard mixed solution series-2 and water.

8.2.5 Calculation Obtain the concentration of sodium oxide from the working curve prepared in 8.2.6 and calculate the content rate of sodium oxide in sample according to the following formula:

$$\text{Sodium oxide (\%)} = \frac{C \times 10^{-3}}{W} \times \frac{250}{100} \times 100$$

where, C : concentration of sodium oxide in sample solution (B) (mg/100 ml)

W : weighing out amount of sample in 6.2.3 (g)

8.2.6 Preparation of working curve After the operations in accordance with 8.2.4 (1) (2), spray standard mixed solution series-2 of 8.2.2 (4), read out each meter (¹⁸) and prepare the relation curve between the readings of meter and the concentrations of sodium oxide to be the working curve.

Table 6. Example of standard mixed solution series-2

Standard mixed solution Series-2	Aluminium chloride solution additional amount ml	Hydro-chloric acid (1+1) additional amount ml	Sodium oxide solution		Potassium oxide solution	
			Standard solution ml	Concentration mg/100 ml	Standard solution ml	Concentration mg/100 ml
1	10	2	1	0.25	1	0.50
2	10	2	2	0.50	2	1.00
3	10	2	3	0.75	3	1.50
4	10	2	4	1.00	4	2.00
5	10	2	5	1.25	5	2.50
6	10	2	6	1.50	6	3.00
7	10	2	7	1.75	7	3.50
8	10	2	8	2.00	8	4.00
9	10	2	9	2.25	9	4.50
10	10	2	10	2.50	10	5.00

8.3 Atomic absorption method

8.3.1 Summary Take a portion of sample solution (C), utilize an atomic absorption analyzer and measure the absorbance of sodium.

8.3.2 Reagents The reagents shall be as follows:

- (1) Standard mixed solution series-1 Use the same solution as that of 6.3.2 (11).

8.3.3 Apparatus Use an atomic absorption analyzer.

8.3.4 Operation As for the determination operation, take a portion of sample solution (C) obtained in 6.3.5 (4), utilize the light source lamp for sodium of atomic absorption analyzer and measure the absorbance at 589.0 nm in wavelength ⁽¹⁹⁾ ⁽¹³⁾.

Note ⁽¹⁹⁾ In the case where the concentration of sodium oxide in sample solution is high, 330.2 nm in wavelength may be used.

8.3.5 Calculation Obtain the concentration of sodium oxide from the working curve prepared in 8.3.6 and calculate the content rate of sodium oxide in sample according to the following formula:

$$\text{Sodium oxide (\%)} = \frac{a \times 10^{-3}}{W} \times 100$$

where, a : concentration of sodium oxide in sample solution (C) (mg/100 ml)

W : weighing out amount of sample in 6.3.4 (g)

8.3.6 Preparation of working curve Utilize the light source lamp for sodium, respectively measure the absorbances at 589.0 nm ⁽²⁰⁾ in wavelength of standard mixed solution series-1 of 6.3.2 (11) and prepare the relation curve between the absorbances and the concentrations of sodium oxide to be the working curve.

Note ⁽²⁰⁾ When 330.2 nm in wavelength is used for measurement of the absorbance of sample solution (C), standard mixed solution series-1 is measured at 330.2 nm in wavelength, too.

9. Method for determination of potassium oxide

9.1 Classification of methods The method for determination of potassium oxide shall be in accordance with either one of the following methods:

- (1) Flame method
(2) Atomic absorption method

9.2 Flame method

9.2.1 Summary Take a portion of sample solution (B), utilize a flame photometer and measure the intensity of emission line of potassium.

9.2.2 Reagents Use the same reagents as those of standard mixed solution series-2.

9.2.3 Apparatus Use a flame photometer.

9.2.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Regulate the measuring wavelength of flame photometer at 767 nm ⁽²¹⁾.
- (2) Carry out the operation in accordance with the procedure of 8.2.4 (2).
- (3) Spray a portion of sample solution obtained in 6.2.4 (4) and take out the reading of meter ⁽¹⁸⁾.

Note ⁽²¹⁾ A potassium filter may be used.

9.2.5 Calculation Obtain the concentration of potassium oxide from the working curve prepared in 9.2.6 and calculate the content rate of potassium oxide in sample according to the following formula:

$$\text{Potassium oxide (\%)} = \frac{C \times 10^{-3}}{W} \times \frac{250}{100} \times 100$$

where, C : concentration of potassium oxide in sample solution (B) (mg/100 ml)

w : weighing out amount of sample in 6.2.3 (g)

9.2.6 Preparation of working curve After operating in accordance with 9.2.4 (1) and (2), spray standard mixed solution series-2 of 8.2.2 (4), read out each meter ⁽¹⁸⁾ and prepare the relation curve between the readings of meter and the concentrations of potassium oxide to be the working curve.

9.3 Atomic absorption method

9.3.1 Summary Take a portion of sample solution (C), utilize an atomic absorption analyzer and measure the absorbance of potassium.

9.3.2 Reagents Use the same reagents as those of 8.3.2.

9.3.3 Apparatus Utilize an atomic absorption analyzer.

9.3.4 Operation As for the determination operation, take a portion of sample solution (C) obtained in 6.3.5 (4), utilize the light source lamp for potassium of atomic absorption analyzer and measure the absorbance at 766.5 nm ⁽²²⁾ in wavelength ⁽¹³⁾.

Note ⁽²²⁾ When the concentration of potassium oxide in sample solution is high, a wavelength of 404.4 nm may be used.

9.3.5 Calculation Obtain the concentration of potassium oxide from the working curve prepared in 9.3.6 and calculate the content rate of potassium oxide in sample according to the following formula:

$$\text{Potassium oxide (\%)} = \frac{C \times 10^{-3}}{W} \times 100$$

where, C : concentration of potassium oxide in sample solution (C) (mg/100 ml)

W : weighing out amount of sample in 6.3.4 (g)

9.3.6 Preparation of working curve Utilize the light source lamp for potassium, respectively measure ⁽²³⁾ the absorbances at 766.5 nm in wavelength of standard mixed solution series-1 of 6.3.2 (11) and prepare the relation curve between the obtained absorbances and the concentrations of potassium oxide to be the working curve.

Note ⁽²³⁾ When 404.4 nm in wavelength is used for measurement of the absorbance of sample solution (C), standard mixed solution series-1, too, is measured at 404.4 nm in wavelength.

10. Method for determination of manganese monoxide

10.1 Classification of method The method for determination of manganese monoxide shall be in accordance with ammonium persulfate oxidation absorptiometry.

10.2 Ammonium persulfate oxidation absorptiometry

10.2.1 Summary Decompose a sample with hydrofluoric acid and sulfuric acid. After evaporating it to dryness, fuse it with sodium carbonate and boric acid and dissolve it with sulfuric acid. Add phosphoric acid and silver nitrate, oxidize it with ammonium persulfate, color reddish purple permanganate ion and measure the absorbance.

10.2.2 Reagents The reagents shall be as follows:

- (1) Sulfuric acid (1 + 1)
- (2) Nitric acid
- (3) Hydrofluoric acid (46 %)
- (4) Sodium carbonate (anhydrous)
- (5) Boric acid
- (6) Phosphoric acid (1 + 1)
- (7) Silver nitrate solution (1 w/v %)
- (8) Ammonium persulfate solution (10 w/v %) Prepare it at each service.

- (9) Standard manganese monoxide solution (0.01 mg MnO/ml) Dissolve 0.224 g potassium permanganate with 100 ml water and add 1 ml sulfuric acid (1 + 1). Then, reduce it by adding 0.5 g sodium hydrogensulfite and expel excess sulfurous acid by boiling. After cooling, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Accurately dilute it ten times with water at each service.

Otherwise, add 10 ml sulfuric acid (1 + 3) to 0.155 g electrolytic metallic manganese and dissolve it by heating. After cooling, transfer it into a one mark volumetric flask of 1000 ml and dilute it up to the marked line with water. Accurately dilute it 20 times with water at each service.

10.2.3 Weighing out amount of sample Weigh out 0.5 g of sample.

10.2.4 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample onto a platinum pan (for example, No. 75), moisten it with water, add 3 ml sulfuric acid (1 + 1), 2 ml nitric acid and 10 ml hydrofluoric acid, sufficiently mix them by stirring with platinum wire, carefully decompose it by heating on a sand bath and evaporate it until white fume of sulfuric acid starts to be generated.
- (2) After standing to cool, wash the inside wall of platinum pan with water and evaporate it to dryness by heating again.
- (3) Add 2.5 g sodium carbonate and 0.5 g boric acid, at first heat it at a low temperature, gradually raise temperature and fuse it by igniting at about 1000°C for about 10 min.
- (4) After standing to cool, add 10 ml sulfuric acid (1 + 1). After dissolving it by heating on a water bath, transfer it into a beaker (100 ml).
- (5) After controlling the amount of solution at about 50 ml, add 2 ml phosphoric acid (1 + 1), 5 ml silver nitrate solution and 10 ml ammonium persulfate solution and boil the solution for about 1 min.
- (6) After cooling it in running water, transfer it into a one mark volumetric flask of 100 ml and dilute it up to the marked line with water.
- (7) Take a portion of this solution into the absorption cell of a photometer and measure the absorbance at nearly 525 nm in wavelength.

10.2.5 Calculation Obtain the amount of manganese monoxide from the working curve prepared in 10.2.6 and calculate the content rate of manganese monoxide in sample according to the following formula:

$$\text{Manganese monoxide (\%)} = \frac{a}{W} \times 100$$

where, a : detection amount of manganese monoxide in
10.2.4 (7) (g)

W : weighing out amount of sample (g)

10.2.6 Preparation of working curve Stepwise take 0 to 30 ml standard manganese monoxide solution (0 to 0.3 mg as manganese monoxide) into beakers (100 ml), add 10 ml sulfuric acid (1 + 1) to each of them, operate that in accordance with the procedures of 10.2.4 (5) to (6) and prepare the relation curve between the obtained absorbances and the amounts of manganese monoxide to be the working curve.

B. Chemical analysis of silica brick and silica refractory mortar

1. Method for determination of ignition loss

1.1 Classification of method The method for determination of ignition loss shall be in accordance with gravimetric method.

1.2 Gravimetric method

1.2.1 Summary Measure the loss when a sample is ignited at about 1050°C to constant weight.

1.2.2 Weighing out amount of sample Weigh out 1 g of sample.

1.2.3 Operation Carry out the determination operation in accordance with the following procedures:

- (1) Weigh out sample into a platinum crucible (for example, No. 30) (24), cover it with slightly leaving the clearance, ignite it at about 1050°C in an electric furnace for about 1 h and let it stand to cool in a desiccator. Thereafter, measure its mass.

Note (24) A porcelain crucible (for example, PC 1 type A 15 ml) may be used.

- (2) Repeat the operation for about each 15 min and obtain the loss when it has become constant weight.

1.2.4 Calculation Calculate the ignition loss of sample according to the following formula:

$$\text{Ignition loss (\%)} = \frac{w}{W} \times 100$$

where, w : loss (g)

W : weighing out amount of sample (g)

2. Method for determination of silicon dioxide

2.1 Classification of methods The method for determination of silicon dioxide shall be in accordance with either one of the following methods:

- (1) Dehydration gravimetric absorptiometric combined method
- (2) Aggregation gravimetric absorptiometric combined method
- (3) Method for calculation by 100 % subtraction

2.2 Dehydration gravimetric absorptiometric combined method

2.2.1 Summary After fusing a sample with sodium carbonate, dissolve it with hydrochloric acid and dehydrate silicic acid by evaporating it to dryness. Thereafter, dissolve the soluble salts with hydrochloric acid and filter it. Ignite the precipitate to be measured and add hydrofluoric acid. After evaporating silicon dioxide, ignite it again to be measured and obtain the amount of main silicon dioxide from the loss thereof. Separately take the filtrate and obtain the amount of residual silicon dioxide by molybdenum blue absorptiometry. Allow the sum of both amounts to be the total amount of silicon dioxide.

2.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1 + 1, 1 + 4, 1 + 50)
- (3) Potassium disulfate (Preliminarily fuse it. After cooling, grind it to be used.)
- (4) Hydrofluoric acid (46 %)
- (5) Hydrofluoric acid (1 + 9) Allow it to be that from which silicohydrofluoric acid is adsorbed to be removed by passing it through C1 type strong basic ion exchange column (Use the chromatographic-tube made of plastics.). Reserve it in a plastic bottle.
- (6) Sulfuric acid (1 + 1)
- (7) Boric acid (4 w/v %) Reserve it in a plastic bottle.
- (8) Sodium carbonate (anhydrous)
- (9) Ammonium molybdate solution Dissolve 10 g ammonium molybdate (4 hydrate) with water to 100 ml. If necessary, filter it and reserve it in a plastic bottle. However, when molybdic acid is deposited during storage, prepare it newly.
- (10) Tartaric acid solution Dissolve 10 g tartaric acid with water to 100 ml and reserve it in a plastic bottle.
- (11) Ascorbic acid solution (5 w/v %) Reserve it in a cool dark place. It is preferable not to use the solution for which more than one month has elapsed after preparation.