



JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS R 5202 : 2010

(JCA)

**Methods for chemical analysis of
cements**

ICS 91.100.10

Reference number : JIS R 5202 : 2010 (E)

PROTECTED BY COPYRIGHT

Date of Establishment: 1950-07-17

Date of Revision: 2010-02-22

Date of Public Notice in Official Gazette: 2010-02-22

Investigated by: Japanese Industrial Standards Committee
Standards Board
Technical Committee on Civil Engineering

JIS R 5202:2010, First English edition published in 2011-08

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 2011

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

PROTECTED BY COPYRIGHT

Contents

	Page
Introduction.....	1
1 Scope	1
2 Normative references	2
3 General requirements for testing	2
3.1 Number of tests	2
3.2 Tolerance	2
3.3 Expression of masses, volumes, factors and results	2
3.4 Ignition	3
3.5 Glass apparatus	3
3.6 Other general requirements	3
4 Preparation of a test sample of cement	3
5 Determination of loss on ignition	3
5.1 Principle	3
5.2 In the case of other than portland blast-furnace slag cement and blast-furnace slag	3
5.3 In the case of portland blast-furnace slag cement and blast-furnace slag	4
5.4 Tolerance	5
6 Determination of residue insoluble in hydrochloric acid and sodium carbonate	5
6.1 Principle	5
6.2 Reagents	5
6.3 Sampling amount	5
6.4 Procedure	5
6.5 Calculation	6
6.6 Tolerance	6
7 Determination of silicon dioxide	6
7.1 Principle	6
7.2 Reagents	7
7.3 Sampling amount	7
7.4 Procedure	7
7.5 Calculation	7
7.6 Tolerance	8
8 Determination of aluminium oxide	8
8.1 Principle	8
8.2 Reagents	8

8.3	Apparatus for photometric titration	9
8.4	Procedure	9
8.5	Blank test	10
8.6	Calculation	10
8.7	Tolerance	11
9	Determination of iron (III) oxide	11
9.1	Principle	11
9.2	Reagents	11
9.3	Apparatus	11
9.4	Procedure	11
9.5	Construction of calibration curve	12
9.6	Calculation	12
9.7	Tolerance	12
10	Determination of calcium oxide	12
10.1	Determination by using indicator for calcium	12
10.2	Determination by calcein indicator or calcein-PPC indicator	16
11	Determination of magnesium oxide	18
11.1	Principle	18
11.2	Reagents	18
11.3	Apparatus	19
11.4	Procedure	19
11.5	Construction of calibration curve	19
11.6	Calculation	19
11.7	Tolerance	20
12	Determination of sulfur trioxide	20
12.1	Principle	20
12.2	Reagent	20
12.3	Procedure	20
12.4	Calculation	20
12.5	Tolerance	21
13	Determination of sodium oxide and potassium oxide	21
13.1	Atomic absorption spectrometry	21
13.2	Flame photometry	23
14	Determination of titanium (IV) oxide	25
14.1	Principle	25
14.2	Reagents	25
14.3	Procedure	26
14.4	Construction of calibration curve	26
14.5	Calculation	26
14.6	Tolerance	26
15	Determination of phosphorus (V) oxide	27

15.1	Principle	27
15.2	Reagents	27
15.3	Procedure	27
15.4	Construction of calibration curve	28
15.5	Calculation	28
15.6	Tolerance	28
16	Determination of manganese (II) oxide	28
16.1	Atomic absorption spectrometry	28
16.2	Absorptiometry	30
17	Determination of sulfur in sulfide	32
17.1	Principle	32
17.2	Direct titration using potassium iodate standard solution	32
17.3	Back titration method using sodium thiosulfate standard solution	34
17.4	Tolerance	36
18	Determination of chlorine	36
18.1	Potentiometric titration	36
18.2	Absorptiometry by mercury (II) thiocyanate	39
18.3	Back titration method using ammonium thiocyanate solution	42
Annex A (informative)	Chemical analysis of major elements of cement by complete analysis	44
Annex B (informative)	Determination of residue insoluble in hydrochloric acid and potassium hydroxide	69
Bibliography		71
Annex JA (informative)	Comparison table between JIS and corresponding International Standard	72
Annex JB (informative)	Table of comparison between current and previous editions of this JIS on technically significant revisions	86

Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry, through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Cement Association (JCA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14. Consequently **JIS R 5202:1999** is replaced with this Standard.

This **JIS** document is protected by the Copyright Law.

Attention is drawn to the possibility that some parts of this Standard may conflict with a patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have technical properties. The relevant Minister and the Japanese Industrial Standards Committee are not responsible for identifying the patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have the said technical properties.

Methods for chemical analysis of cements

Introduction

This Japanese Industrial Standard was established in 1950 and has been revised ten times up to the present, and the last revision was made in 1999. This Standard specifies the methods for the analysis of cement by wet chemistry.

The International Standard for analysis methods of cements by wet analysis, **ISO 29581-1**, which was published as the first edition on March 15th, 2009, specifies the procedure of complete decomposition of cement for chemical analysis of major elements of cement [silicon dioxide, aluminium oxide, iron (III) oxide, calcium oxide and magnesium oxide].

On the other hand, this **JIS** Standard specifies the procedure for dissolution of cement by acid and determination of contents of the dissolved components, and is to be cited and used for determination of components in each of the quality standards of cement (**JIS R 5210**, **JIS R 5211**, **JIS R 5212**, **JIS R 5213** and **JIS R 5214**).

Therefore, this **JIS** Standard only adopts, from among the methods specified in the said International Standard, the analysis method in which cement is dissolved by acid, while adding some analysis methods that are not given in the International Standard.

Portions with continuous sidelines or dotted underlines are the matters in which the contents of the corresponding International Standard have been modified. A list of modifications with explanations is given in Annex JA. Further, a comparison table between the previous and current editions of this JIS on technically significant revisions is shown in Annex JB.

1 Scope

This Standard specifies the methods for the analysis of cement¹⁾ by wet chemistry.

It is also applicable to analysis of clinkers and blast-furnace slag to be used for manufacture of blast-furnace slag cement.

NOTE : The International Standard corresponding to this Standard and the symbol of degree of correspondence are as follows:

ISO 29581:2009 *Cement—Test methods—Part 1: Analysis by wet chemistry* (MOD)

The symbols which denote the degree of correspondence in the contents between **JIS** and the corresponding International Standard are **IDT** (identical), **MOD** (modified) and **NEQ** (not equivalent) according to **ISO/IEC Guide 21-1**.

Note ¹⁾ “Cement”, for the purpose of this Standard, is portland cement specified in **JIS R 5210**, portland blast-furnace slag cement specified in **JIS R 5211**, portland pozzolan cement specified in **JIS R 5212**, portland fly-ash cement specified in **JIS R 5213**, and ecocement specified in **JIS R 5214**.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS K 0050	<i>General rules for chemical analysis</i>
JIS K 0113	<i>General rules for methods of potentiometric, amperometric, coulometric, and Karl Fischer titrations</i>
JIS K 0115	<i>General rules for molecular absorptiometric analysis</i>
JIS K 0121	<i>General rules for atomic absorption spectrometry</i>
JIS K 8005	<i>Reference materials for volumetric analysis</i>
JIS K 8102	<i>Ethanol (95) (Reagent)</i>
JIS P 3801	<i>Filter paper (for chemical analysis)</i>
JIS R 3503	<i>Glass apparatus for chemical analysis</i>
JIS R 3505	<i>Volumetric glassware</i>
JIS R 5204	<i>Chemical analysis method of cement by x-ray fluorescence</i>
JIS Z 8401	<i>Guide to the rounding of numbers</i>
JIS Z 8801-1	<i>Test sieves—Part 1: Test sieves of metal wire cloth</i>

3 General requirements for testing

3.1 Number of tests

The number of tests performed on one identical sample shall be two, except where the analysis is one of a series subject to statistical control, in which case a single test shall be the minimum required.

3.2 Tolerance

When the difference between the two tests exceeds the specified tolerance, a retest shall be conducted, and two most adjacent test results shall be averaged and reported as the analysis results (see 3.3).

3.3 Expression of masses, volumes, factors and results

Express masses in grams to the nearest 0.000 1 g and volumes from burettes in milliliters to the nearest 0.01 ml.

Express the factors of solutions given by the mean of three measurements.

Express each analysis result, except for that of chlorine (Cl), as a percentage generally to two decimal places according to 2 b) of JIS Z 8401. The analysis result of chlorine (Cl) shall be expressed as a percentage to three decimal places.

Express the results, where two test results have been obtained, as the mean of the results, as a percentage generally to two decimal places according to Rule A in 2 c) of JIS Z 8401, except for analytical items of chlorine (Cl). Express the results of chlorine (Cl) as a percentage to three decimal places.

3.4 Ignition

Carry out the ignition as follows:

Place the filter paper and its precipitate (residue) into a crucible which has been previously ignited and tared. Dry it, then incinerate slowly in an oxidizing atmosphere in order to avoid immediate flaming, while ensuring complete incineration. Ignite the crucible and its contents at the stated temperature, then allow to cool to the laboratory temperature in a desiccator. Weigh the crucible and its contents.

3.5 Glass apparatus

Glass apparatus used for performing the analysis shall be in accordance with **JIS R 3503** and **JIS R 3505**.

3.6 Other general requirements

General requirements other than stated above shall be in accordance with **JIS K 0050**, **JIS K 0113**, **JIS K 0115** and **JIS K 0121**.

4 Preparation of a test sample of cement

Take, for preparing test sample, cement from a unit of inspection such that the taken portion represents the average quality of the unit, and divide it to obtain representative sample of about 5 kg. The sampling and dividing method shall be agreed upon between the purchaser and the supplier. Take approximately 100 g of the laboratory sample by means of a sample divider or by quartering. Sieve this portion on a 150 μm or 125 μm sieve as specified in **JIS Z 8801-1**. Remove metallic iron from the material retained on the sieve by means of a magnet. Then grind the iron-free fraction of the retained material so that it completely passes the 150 μm or 125 μm sieve. Transfer the sample to a clean, dry container with an airtight closure and shake vigorously to mix it thoroughly.

Carry out all operations as quickly as possible to ensure that the test sample is exposed to ambient air only for the minimum time.

5 Determination of loss on ignition

5.1 Principle

The loss on ignition is determined in an oxidizing atmosphere (air). By igniting the sample in air at $950\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$, the carbon dioxide and water are driven off and any oxidizable elements present are oxidized to some extent. The error resulting from the oxidation of metallic iron, iron (II) oxide or bivalent manganese (II) oxide is usually considered negligible and only the correction for the extent of oxidation of any sulfides is applied.

5.2 In the case of other than portland blast-furnace slag cement and blast-furnace slag

5.2.1 Procedure

- Weigh approximately 1 g²⁾ of sample, correctly to 0.000 1 g, into a platinum or porcelain crucible which has been previously ignited and tared.

- b) Place the cover on the crucible, sliding off a little to make some clearance, and place the crucible in the electric furnace controlled at $950\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$, and ignite for 15 min.
- c) Allow the crucible to cool to room temperature in a desiccator and weigh the mass.
- d) Repeat this ignition, of 15 min each, to determine the constant mass. The constant mass is known to be reached when the mass difference between before and after ignition is less than 0.000 5 g.

If any gain in mass has occurred in the determination of the constant mass, the mass before the gain shall be employed. If the mass has gained at the first 15 min ignition, it shall be noted simply as “+”.

Note ²⁾ In the corresponding International Standard, the sampling range is specified to be $1.00\text{ g} \pm 0.05\text{ g}$.

5.2.2 Calculation

Calculate the loss on ignition from the following formula:

$$ig.loss = \frac{m - m'}{m} \times 100$$

where, *ig.loss* : loss on ignition (%)

m : mass of sample (g)

m' : mass of sample after ignition (g)

5.3 In the case of portland blast-furnace slag cement and blast-furnace slag

5.3.1 Procedure

- a) Perform the procedures in **5.2.1 a)** to **d)** and determine the apparent loss on ignition [*ig.loss* (ap)] by the formula in **5.2.2**.
- b) Determine the content of sulfur trioxide in sample before ignition [SO_3 (B)] according to clause **12**.
- c) Determine the content of sulfur trioxide in sample after ignition [SO_3 (A)] according to the following procedure.

Weigh 2 g to 3 g of sample into a crucible, and ignite it according to **5.2.1 b)** to **d)**.

The constant mass shall be confirmed when the mass difference between before and after the ignition is less than 0.05 %. Using this ignited sample³⁾, determine the sulfur trioxide content according to the procedure in clause **12**.

For the sulfur trioxide content after ignition, the value of sulfur trioxide of glass bead determined according to **JIS R 5204** may be adopted.

Note ³⁾ For weighing out the sample after ignition, the lump of sample should be broken down into uniform structure, and then quickly weighed out.

5.3.2 Calculation

Calculate the loss on ignition in the sample from the following formula:

$$ig.loss = ig.loss(ap) + 0.8 \times [SO_3(A) - SO_3(B)]$$

where, $ig.loss$: loss on ignition (%)

$ig.loss(ap)$: apparent loss on ignition (%)

$SO_3(A)$: sulfur trioxide content in sample after ignition (%)

$SO_3(B)$: sulfur trioxide content in sample before ignition (%)

5.4 Tolerance

The tolerance shall be 0.10 %.

6 Determination of residue insoluble in hydrochloric acid and sodium carbonate

6.1 Principle

This determination method is a conventional method in which the insoluble residue in cement is obtained by treating the sample with a dilute hydrochloric acid solution so that the precipitation of soluble silicon dioxide is minimum. The residue from this treatment is treated with a boiling solution of sodium carbonate in order to re-dissolve traces of silicon dioxide which may have been precipitated. The residue is determined gravimetrically after ignition.

6.2 Reagents

The following reagents shall be used:

- Hydrochloric acid (1+1)**
- Sodium carbonate solution (50 g/L)**
- Methyl red indicator (2 g/L)** Dissolve 0.2 g of methyl red in 100 ml of ethanol specified in **JIS K 8102**.

6.3 Sampling amount

Weigh out approximately 1 g⁴⁾ of sample to the nearest 0.000 1 g.

Note ⁴⁾ In the corresponding International Standard, the sampling range is specified to be 1.00 g ± 0.05 g.

6.4 Procedure

Perform the determination according to the following procedures.

- Place the sample in a dry 200-ml beaker, add about 20 ml of water and while stirring with a glass rod to disperse the sample, add 10 ml of hydrochloric acid (1+1) to dissolve. If necessary, heat the solution gently and crush the undissolved lumps of sample with the flattened end of the glass stirring rod until decomposition of the cement is complete.
- Add warm water to make 50 ml, cover with a watch glass, and heat on water bath for 10 min.

- c) Filter⁵⁾ by using the filter paper (Class 5 B, 110 mm) conforming to **JIS P 3801** and wash it with warm water 8 times. Receive the filtrate and washings in a 500-ml beaker and cool it down to the room temperature. Then wash it into a 250-ml volumetric flask, make up to the mark with water and shake to mix it. Take this solution as the sample solution (F) and use it for the determination of sulfur trioxide and titanium (IV) oxide.

Moreover, when the determination of titanium (IV) oxide is not carried out, preserve the filtrate and washings received in beaker as it is and use it for the determination of sulfur trioxide.

- d) Remove the filter paper from the funnel and place it back in the 200-ml beaker. Add 50 ml of sodium hydroxide solution (50 g/L), stir to dissolve the filter paper and after covering with a watch glass, heat on water bath for 15 min.
- e) Add one or two drops of methyl red indicator, and neutralize it by adding gradually hydrochloric acid (1+1). When the colour of the solution has changed from yellow to red, add further 2 drops to 3 drops.
- f) Filter the solution with a filter paper (Class 5 B, 110 mm) conforming to **JIS P 3801**, and wash with warm water 10 times.
- g) Dry the residue in a crucible, and after gradually heating to incinerate the filter paper, ignite in an electric furnace controlled at a temperature of $950\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ for 30 min. After allowing to cool in a desiccator, weigh the mass.

Note ⁵⁾ If it is anticipated that a part of the sample can remain undissolved, put adequate amount of powder filter paper in the funnel before filtering.

6.5 Calculation

Calculate the content of insoluble residue from the following formula:

$$insol. = \frac{m'}{m} \times 100$$

where, *insol.* : mass of insoluble residue (%)

m : mass of sample (g)

m' : mass of residue (g)

6.6 Tolerance

The tolerance shall be 0.10 %.

7 Determination of silicon dioxide

7.1 Principle

Sample is dissolved with perchloric acid, heated on a sand bath to dehydrate silicon dioxide, and made insoluble. Hydrochloric acid is added to the sample to dissolve the dissolvable salts, and then the solution is filtered. The precipitate is ignited and the mass is weighed, and the content of silicon dioxide is determined.

7.2 Reagents

The following reagents shall be used:

- a) **Perchloric acid (60 %)**
- b) **Hydrochloric acid (1+1)**

7.3 Sampling amount

Weigh accurately about 1 g of sample to the nearest 0.000 1 g.

7.4 Procedure

Perform the determination according to the following procedures:

- a) Place the sample in a dry 100-ml beaker, add 10 ml of perchloric acid (60 %), and agitate it with a glass rod to dissolve it.
- b) Heat it on a sand bath⁶⁾ to evaporate moisture with cares to avoid spattering, and when white fumes of perchloric acid emit, cover it with a watch glass⁷⁾, and heat it for another 5 min with the bottom of the beaker sunk in sand.
- c) Remove the beaker from the sand bath, allow it to cool, take off the watch glass after rinsing with water, add 5 ml of hydrochloric acid (1+1) and about 20 ml of warm water, agitate it, and smash jelly-like large lumps.
- d) Filter it through a filter paper (Class 5 B, 110 mm) conforming to **JIS P 3801**, and wash 10 to 12 times with warm water. Receive the filtrate in a 500-ml beaker, and after allowing to cool to the laboratory temperature, wash it into a 250-ml volumetric flask. Make up to the mark with water and shake to mix. Take this solution as sample solution (A), and employ it for determination of aluminium oxide or others.
- e) Place the precipitate in a crucible, dry it, heat gradually to ash the filter paper with cares not to let flame emit. Ignite it for 1 h in an electric furnace controlled at $1\,175\,^{\circ}\text{C} \pm 25\,^{\circ}\text{C}$ ⁸⁾, allow it to cool in a desiccator, and then weigh its mass.

Notes ⁶⁾ The temperature of the sand bath should be controlled such that the thermometer inserted into the mid-depth of the sand shows approximately 180 °C.

⁷⁾ If the cover is placed from the beginning, water drops of condensation on the watch glass may drop and cause the content of the crucible to scatter.

⁸⁾ Ignition may be performed at $1\,050\,^{\circ}\text{C} \pm 25\,^{\circ}\text{C}$.

7.5 Calculation

Calculate the content of silicon dioxide from the following formula:

$$\text{SiO}_2 = \frac{m'}{m} \times 100 - \text{insol.}$$

where, SiO_2 : silicon dioxide content (%)

m' : mass of precipitate (g)

m : mass of sample (g)
 $insol.$: insoluble residue content obtained in clause 6 (%)

7.6 Tolerance

The tolerance shall be 0.20 %.

8 Determination of aluminium oxide

8.1 Principle

An aliquot is taken from the sample solution (A) stored after prepared in 7.4 d), to which surplus amount of EDTA is added to adjust its pH to about 3. The solution is then boiled to complete EDTA complex compound, and after cooling, and its pH being adjusted to 5.5, back-titration with zinc standard solution with the indicator of xylenol orange is performed.

8.2 Reagents

The following reagents shall be used:

- EDTA solution (0.01 mol/L)** Dissolve 3.73 g of disodium ethylenediamine tetraacetate dihydrate in water, transfer into a 1 000-ml volumetric flask, add water to the mark, shake to mix and store in a polyethylene bottle.
- Sodium acetate solution (pH 5.5)** Dissolve 250 g of sodium acetate trihydrate in about 1 L of water and add acetate to adjust the pH to 5.5 by using a pH meter.
- Ammonium acetate solution (200 g/L)**
- Xylenol orange indicator (1 g/L)** Dissolve 0.1 g of 3,3'-bis[*N,N*-di(carboxymethyl)-aminomethyl]-*o*-cresolsulfophthalein in 100 ml of water, put it in a brown coloured bottle, and store in a cold dark place. Prepare this solution newly in every 2 months.
- Zinc standard solution (0.01 mol/L)** Weigh accurately about 0.65 g of zinc of volumetric analysis reference material specified in **JIS K 8005** to the nearest 0.000 1 g into a 300-ml beaker, add about 10 ml of water and 20 ml of hydrochloric acid (1+1), cover with a watch glass and heat on a water bath to dissolve. Remove the watch glass after washing with water, add about 100 ml of water and ammonium acetate solution (200 g/L) and after adjusting the pH to 5.5 using a pH meter, transfer into a 1 000-ml volumetric flask, add water to the mark and shake to mix. Calculate the equivalent amount of aluminium oxide of this standard solution from the following formula, and round the result to seven decimal places:

$$E = \frac{m \times (a/100)}{65.39} \times \frac{1}{1\,000} \times \frac{101.96}{2}$$

where, E : amount of aluminium oxide equivalent to 1 ml of zinc standard solution (0.01 mol/L) (g)

m : mass of zinc (g)

a : purity of zinc (%)

Alternatively, take a V_1 -ml aliquot from the zinc standard solution on the market being traceable to the national measurement standard, transfer it into a V_2 -ml volumetric flask, make up to the mark with water, shake to mix it and prepare so as to make it about 0.01 mol/L in zinc.

Calculate the equivalent amount of aluminium oxide of this standard solution from the following formula, and round the result to seven decimal places:

$$E = \frac{(C/1000) \times V_1}{65.39} \times \frac{1}{V_2} \times \frac{101.96}{2}$$

where, E : amount of aluminium oxide equivalent to 1 ml of zinc standard solution (0.01 mol/L) (g)

C : concentration of zinc standard solution on the market (mg/ml)

V_1 : volume of an aliquot of zinc standard solution on the market (ml)

V_2 : volume of volumetric flask (ml)

8.3 Apparatus for photometric titration

This apparatus is composed of a titration vessel, detector, and dropping device of titrant.

- a) **Titration vessel** The titration vessel is a container used for titration and shall be capable of agitating the solution during titration⁹⁾.
- b) **Detector** The detector shall be capable of measuring the absorbance of the solution at wavelengths of around 530 nm and 650 nm.
- c) **Dropping device of titrant** The dropping device shall be capable of quantitative addition of the titrant¹⁰⁾.

Notes ⁹⁾ It is preferable to use successively the beaker which was used for determination operation.

¹⁰⁾ A burette or automatic burette can be used here.

8.4 Procedure

8.4.1 Visual determination of the end-point

- a) Take a 25-ml aliquot from the sample solution (A), stored after prepared in 7.4 d), using a volumetric pipette into a 300-ml beaker, and further add the EDTA solution (0.01 mol/L) of the amount as given in table 1 according to the content of aluminium oxide, iron (III) oxide and titanium (IV) oxide in the sample by using a volumetric pipette, and add water to make approximately 100 ml.
- b) Add sodium acetate solution (pH 5.5) while agitating until its pH becomes about 3 using a pH meter¹¹⁾, and boil it for about 5 min.
- c) After cooling it, add ammonium acetate solution (200 g/L) until its pH becomes 5.5 using a pH meter.

- d) Drop one or two drops of xylenol orange indicator, titrate it with zinc standard solution (0.01 mol/L)¹²⁾ until the end point where the solution turns reddish tint from yellow.

Notes ¹¹⁾ For controlling the pH, methyl orange indicator may be used.

¹²⁾ Titration should be slow and with sufficient agitation near the end point since the colour change becomes dull towards the end.

Table 1 Addition amount of EDTA solution (0.01 mol/L)

[Aluminium oxide content] + [Iron (III) oxide content] + [Titanium (IV) oxide content] %	Added amount ml
5	10
10	20
15	30

8.4.2 Photometric determination of the end-point

- a) Operate similarly to **8.4.1 a) to c)**.
- b) Drop one or two drops of xylenol orange indicator, titrate it with zinc standard solution (0.01 mol/L) while agitating the solution, measure the absorbance of the solution at each amount of titrant at a wavelength of around 530 nm until the colour of the solution turns red ¹³⁾.
- c) Plot the relation between the amount of titrant and absorbance of the solution, and prepare the titration curve. Find an inflection point or the point where titration curve shows the maximum gradient, and regard the value of the point on the abscissa as the end point ¹⁴⁾.

Apply the same end-point judgment method for the blank test.

Notes ¹³⁾ Increment in the added titrant amount should be by 0.05 ml to 0.10 ml. For blank test, it should be about 0.02 ml to 0.06 ml.

¹⁴⁾ The maximum value of the micro volume (change in absorbance/change in amount of titrant) on the titration curve may be obtained as the end point.

8.5 Blank test

Pour 10 ml of perchloric acid (60 %) and 5 ml of hydrochloric acid (1+1) in a 100-ml beaker, further add about 20 ml of water and mix well. Then wash it into a 250-ml volumetric flask, add water to the mark and shake to mix. Using this instead of the sample solution (A), perform the operation in **8.4**.

8.6 Calculation

Calculate the aluminium oxide content from the following formula:

$$Al_2O_3 = \frac{(V_2 - V_1) \times E}{m} \times \frac{250}{25} \times 100 - (Fe_2O_3 + TiO_2) \times 0.638$$

where, Al_2O_3 : aluminium oxide content (%)

V_1 : volume of zinc standard solution (0.01 mol/L) used in **8.4.1 d)** or **8.4.2 c)** (ml)

V_2 : amount of zinc standard solution (0.01 mol/L) used in **8.5** (ml)

E : amount of aluminium oxide equivalent to 1 ml of zinc standard solution (0.01 mol/L) 1 ml (g)

m : mass of sample in **7.3** (g)

Fe_2O_3 : iron (III) oxide content obtained in clause **9** (%)

TiO_2 : titanic (IV) oxide content obtained in clause **14** (%)

8.7 Tolerance

The tolerance shall be 0.20 %.

9 Determination of iron (III) oxide

9.1 Principle

An aliquot is taken from the sample solution (A), stored after prepared in **7.4 d)**, and the absorbance of iron is measured by means of an atomic absorption spectrometer.

9.2 Reagents

The following reagents shall be used:

- a) **Iron (III) oxide standard stock solution (Fe_2O_3 : 1.0 mg/ml)** Weigh out accurately 0.700 g of metallic iron (99.0 % or more), and add about 10 ml of hydrochloric acid (1+1) to dissolve the iron. Transfer it into a 1 000-ml volumetric flask, add water to the mark and shake to mix. Alternatively, dilute an iron standard solution which is traceable to the national measurement standard and available on the market, so as to make it approximately 1 mg/ml in Fe_2O_3 .
- b) **Iron (III) oxide standard solution¹⁵⁾** Dilute ten times the iron (III) oxide standard stock solution. Take aliquots of this solution, increased stepwise from 0 ml to 15 ml, into as many 100-ml volumetric flasks, and to each of them, add the perchloric acid (1+500) to the mark and shake well to mix.

Note ¹⁵⁾ Mixed standard solution may be prepared by an appropriate combination of iron (III) oxide standard stock solution, magnesium oxide standard stock solution, alkali oxide mixed stock solution and manganese (II) oxide standard stock solution.

9.3 Apparatus

An atomic absorption spectrometer shall be used.

9.4 Procedure

Perform the determination according to the following procedures:

- a) Take an aliquot of a certain volume¹⁶⁾ from the sample solution (A) stored after prepared in **7.4 d)** into a 100-ml volumetric flask, add water up to the mark and shake to mix. This solution is used for test solution (B).
- b) Using a light source for iron of the atomic absorption spectrometer, measure the absorbance of the sample solution (B) at the wavelength of 248.3 nm.

The conditions for the apparatus, such as the current in the lamp, slit width of spectrometer, pressure of burning gas or supporting gas, flow rate, and the position of light flux, shall be appropriately established depending on the type of the apparatus. For the shortage of sensitivity, either a scale magnifying device is used or the sensitivity is adjusted by the built-in sensitivity controlling device. When the sensitivity is unnecessarily high, it shall be reduced by adjusting the angle of light flux.

Note ¹⁶⁾ The volume of the aliquot taken here shall depend upon on the content of iron (III) oxide and the type of the apparatus used. Normally, typical amount of 10 ml should be taken.

9.5 Construction of calibration curve

Using a light source for iron of the atomic absorption spectrometer, measure each absorbance of the iron (III) oxide standard solution at the wavelength of 248.3 nm and construct a calibration curve.

9.6 Calculation

Obtain the amount of iron (III) oxide in sample solution (B) from the calibration curve constructed in **9.5**, and calculate the content of iron (III) oxide in the sample from the following formula:

$$Fe_2O_3 = \frac{c}{m} \times \frac{250}{v} \times 100$$

where, Fe_2O_3 : iron (III) oxide content (%)

c : amount of iron (III) oxide in sample solution (B)
(g/100 ml)

m : mass of sample in **7.3** (g)

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

9.7 Tolerance

The tolerance shall be 0.10 %.

10 Determination of calcium oxide

10.1 Determination by using indicator for calcium

10.1.1 Principle

An aliquot of the sample solution (A), stored after prepared in **7.4 d)**, is taken, and neutralized with aqueous ammonia, and then the precipitate of hydroxide is filtered. After the filtrate is allowed to cool, potassium hydroxide solution is added to make its

pH 12.7 to 13.2. Then, with the addition of an indicator for calcium, titration with EDTA standard solution is performed.

10.1.2 Reagents

The following reagents shall be used:

- a) **Methyl red indicator (2 g/L)** Prepare similarly to **6.2 c)**.
- b) **Aqueous ammonia (1+1)**
- c) **Ammonium nitrate solution (20 g/L)**
- d) **Triethanolamine (1+1)**
- e) **Potassium hydroxide solution (approximately 3 mol/L)** Dissolve 200 g of potassium hydroxide in water to make total 1 000 ml.
- f) **Indicator for calcium** Mix 0.5 g of 2-hydroxy-1-(2'-hydroxy-4'-sulfo-1'-naphthylazo)-3-naphthoic acid and 50 g of potassium sulfate, and grind them uniformly, and preserve it in a brown bottle.
- g) **Zinc standard solution (0.02 mol/L)** Weigh about 0.65 g of zinc of volumetric analysis reference material specified in **JIS K 8005** to the nearest 0.000 1 g into a 300-ml beaker, add 10 ml of water and 20 ml of hydrochloric acid (1+1), cover it with a watch glass, and dissolve it on a water bath. Wash it into a 500-ml volumetric flask with water, and after allowing it to cool to room temperature, add water up to the mark and shake to mix. Calculate the factor from the following formula, and round off the result to four decimal places:

$$f = \frac{m \times a}{0.6539 \times 100}$$

where, f : factor of zinc standard solution (0.02 mol/L)

m : mass of zinc (g)

a : purity of zinc (%)

- h) **Buffer solution (pH 10)** Dissolve 70 g of ammonium chloride in a suitable amount of water, add 570 ml of aqueous ammonia and add water to make total 1 000 ml.
- i) **EBT indicator** Dissolve 0.2 g of Eriochrome Black T in mixture of 15 ml of triethanolamine and 5 ml of ethanol specified in **JIS K 8102** and preserve in a brown bottle with a dropping pipette.
- j) **EDTA standard solution (0.02 mol/L)** Dissolve 7.5 g of disodium ethylenediamine tetraacetate dihydrate in a suitable amount of water and transfer it into a 1 000-ml volumetric flask. Add water up to the mark, shake to mix, and preserve it in a polyethylene bottle.

10.1.3 Procedure

10.1.3.1 Visual determination of end-point

- a) Standardize EDTA standard solution (0.02 mol/L) as follows:

Take a 25-ml aliquot from the zinc standard solution (0.02 mol/L) and transfer into a 300-ml beaker using a volumetric pipette, and add water to make total about 100 ml. Add buffer solution to control its pH to 9.5 to 10.0 ¹⁷⁾, add two or three drops of EBT indicator, place it on a tungsten lamp illuminator, and titrate it with EDTA standard solution (0.02 mol/L) until the end point where the reddish violet colour of the solution loses its red and turns completely blue.

A tungsten lamp illuminator shall be capable of emitting light, by a tungsten lamp of approximately 30 W, which will penetrate through the solution kept in the beaker through an opal glass or plastics plate. Utilizing the obtained volume of titrant, calculate the amount of calcium oxide equivalent to EDTA standard solution (0.02 mol/L) from the following formula, and round the result to seven decimal places:

$$E = \frac{0.0011216 \times 25 \times f}{v}$$

where, E : amount of calcium oxide equivalent to 1 ml of EDTA standard solution (0.02 mol/L) (g)
 f : factor of zinc standard solution (0.02 mol/L)
 v : volume of EDTA standard solution (0.02 mol/L) used (ml)

Note ¹⁷⁾ Adding about 3 ml of buffer solution gives the specified pH.

- b) Take two 20-ml aliquots into each of two 300-ml beakers from the sample solution (A) which was stored after prepared in **7.4 d**).
- c) Add warm water to each of them to make total about 150 ml and heat them up to near boiling.
- d) Add one or two drops of methyl red indicator, drop gradually aqueous ammonia (1+1) while agitating the solution until the solution turns from red to yellow, and then add 1 or 2 drops.
- e) Boil them for about 1 min and stop heating. Allow the precipitate to settle. Then immediately filter them through a filter paper (Class 5 A, 110 mm) conforming to **JIS P 3801**, and wash 8 times with ammonium nitrate warm solution (20 g/L). Receive the filtrate respectively in two 500-ml beakers, and discard the precipitate.

Ammonium nitrate solution (20 g/L) shall be used after the solution, in which two or three drops of methyl red indicator was added, turned from red to yellow by adding aqueous ammonia (1+1). If heating this solution turns back to red colour, add aqueous ammonia to make it yellow, and then use it.

- f) When the sample is portland blast-furnace slag cement or blast-furnace slag, it is necessary to remove manganese from the filtrate by the following procedures.

After the filtrate was made weak acid by adding hydrochloric acid (1+1), heat it to concentrate to about 150 ml, add 5 ml of saturated bromine solution and 10 ml of aqueous ammonia (1+1), and boil it for at least 5 min. After the coagulation of precipitate makes the solution transparent, filter the coagulation through a filter

paper (Class 5 B, 110 mm) conforming to **JIS P 3801**, and wash 7 to 8 times with warm water. Add hydrochloric acid (1 + 1) to the filtrate to make it acidic, and boil it to eliminate bromine completely.

- g) Concentrate the filtrate to about 200 ml, and allow them to cool to room temperature.
- h) Into the filtrate obtained from the one beaker, add 2 ml of triethanolamine (1 + 1) and potassium hydroxide solution (approximately 3 mol/L) until its pH is adjusted to 12.7 to 13.2¹⁸⁾ by means of a PH meter.
- i) After standing it for 2 or 3 min, add 0.1 g of the indicator for calcium, place it on a tungsten lamp illuminator, titrate it with EDTA standard solution (0.02 mol/L) until the end point where the solution turns completely from reddish violet to blue. The value thus obtained shall be the preliminary titration value.

A tungsten lamp illuminator shall be capable of emitting light, by a tungsten lamp of approximately 30 W, which will penetrate through the solution kept in the beaker through an opal glass or plastics plate.

- j) Into the other filtrate, add 2 ml of triethanolamine (1 + 1), agitate it, drop EDTA standard solution (0.02 mol/L) from a burette, and stop its dropping once at the point where dropped volume is less than the preliminary volume at **i)** by 1 ml to 2 ml.
- k) Add potassium hydroxide solution (approximately 3 mol/L) whose volume is the same as **h)** in it, and agitate. After standing it for 2 or 3 min, add 0.1 g of indicator for calcium, and titrate it with EDTA standard solution (0.02 mol/L) similarly to the procedures in **i)**.

Note ¹⁸⁾ In this time, if the pH of the solution is outside the range of 12.7 to 13.2, the result will become inaccurate. About 7 ml of potassium hydroxide (approximately 3 mol/L) gives the specified pH value.

10.1.3.2 Photometric determination of the end-point

- a) Standardize EDTA standard solution (0.02 mol/L) using an apparatus for photometric titration specified in **8.3** according to the following procedure:

Take a 25-ml aliquot of zinc standard solution (0.02 mol/L) with a volumetric pipette into a 300-ml beaker, add water to make total about 100 ml. Add buffer solution to control its pH to 9.5 to 10.0¹⁷⁾, add 2 or 3 drops of EBT indicator, and titrate it with EDTA standard solution (0.02 mol/L) while agitating it. At every titration volume measure the absorbance of the solution at a wavelength of around 650 nm until the solution turns completely blue¹⁹⁾ After completion of the titration, plot the volume of titration and the absorbance of the solution to prepare the titration curve, find an inflection point or the point where the titration curve shows the maximum gradient, and regard its value on the abscissa as the end point¹⁴⁾. Utilizing this volume of titrant, calculate the amount of calcium oxide equivalent to EDTA standard solution (0.02 mol/L) according to the formula shown in **10.1.3.1 a)**, and round off the obtained result to seven decimal places.

- b) Operate according to **10.1.3.1 b)** to **j)**.

- c) Add potassium hydroxide solution (approximately 3 mol/L) by the same amount as in **10.1.3.1 h)**, agitate it, and allow it to stand for 2 or 3 min. Add 0.1 g of the indicator for calcium, titrate it with EDTA standard solution (0.02 mol/L) while agitating it using the apparatus for photometric titration specified in **8.3**, and at every titration volume. Measure the absorbance of the solution at a wavelength of around 650 nm.
- d) When the solution turns completely blue, carry out over-titration by a volume of about 1 ml, and end the measurement ²⁰⁾.
- e) Plot the relation between the volume of titration and the absorbance. Prepare a titration curve, and find an inflection point or the point where the titration curve shows the maximum gradient, and regard its value on the abscissa as the end point ¹⁴⁾.

Notes ¹⁹⁾ It is preferable to make titration interval from 0.02 ml to 0.04 ml.

²⁰⁾ It is preferable to make titration interval from 0.04 ml to 0.08 ml.

10.1.4 Calculation

Calculate the content of calcium oxide in sample from the following formula:

$$CaO = \frac{v \times E}{m} \times \frac{250}{20} \times 100$$

where, CaO : calcium oxide content (%)

v : consumed volume of EDTA standard solution (0.02 mol/L), determined in **10.1.3.1 k)** or **10.1.3.2 e)** (ml)

E : amount of calcium oxide equivalent to 1 ml of EDTA standard solution (0.02 mol/L), determined in **10.1.3.1 a)** or **10.1.3.2 a)** (g)

m : mass of sample in **7.3** (g)

10.1.5 Tolerance

The tolerance shall be 0.25 %.

10.2 Determination by calcein indicator or calcein-PPC indicator

10.2.1 Principle

An aliquot is taken from the sample solution (A), stored after prepared in **7.4 d)**, and potassium hydroxide solution is added to control its pH to 12.7 to 13.2. Then, with addition of calcein indicator or calcein-PPC indicator, titration with EDTA standard solution is performed.

10.2.2 Reagents

The following reagents shall be used:

- a) **Triethanolamine (1+1)**
- b) **Potassium hydroxide solution (approximately 3 mol/L)** Prepare according to **10.1.2 e)**.

- c) **Calcein indicator** Mix and pulverize 0.10 g of calcein {3,3'-bis[N,N-di(calboxy methyl)-amino methyl]-fluorescein} together with 10 g of potassium sulfate, make it uniform and preserve in a brown bottle.
- d) **Calcein-PPC indicator** Mix 0.08 g of calcein {3,3'-bis[N,N-di(calboxy methyl)-amino methyl]-fluorescein}, 0.02 g of 3,3'-bis[N,N-di(calboxy methyl)-amino methyl]-phenolphthalein, and 10 g of potassium sulfate and grind them together to make uniform powder and preserve in a brown bottle.
- e) **EDTA standard solution (0.02 mol/L)** Prepare according to **10.1.2 j**).

10.2.3 Procedure

10.2.3.1 Visual determination of the end-point

- a) Standardize the EDTA standard solution (0.02 mol/L) according to **10.1.3.1 a**).
- b) Take 20-ml aliquots from the sample solution (A), stored after prepared in **7.4 d**), into each of two 300-ml beakers using a volumetric pipette, and add water to make about 200 ml.
- c) To one of the beakers obtained above, add 10 ml of triethanolamine (1+1) and potassium hydroxide solution (approximately 3 mol/L) to adjust the pH to 12.7 to 13.2²¹⁾.
- d) After leaving it to stand for 2 min to 3 min, add about 0.05 g of calcein indicator or calcein-PPC indicator, titrate²²⁾ it with EDTA standard solution (0.02 mol/L), and take the point where the colour of the solution changes from fluorescent greenish yellow to orange (non-fluorescent) as the end point in the case of calcein indicator or take the point where the colour of the solution changes from fluorescent greenish yellow to reddish purple (non-fluorescent) as the end point in the case of calcein-PPC indicator. Take the thus obtained values as the preliminary titration value.
- e) To the other beaker, add 10 ml of triethanolamine (1+1), stir, and add the EDTA standard solution (0.02 mol/L) using a burette. Stop the titration when the titrated amount is 1 ml to 2 ml less than the preliminary titration value obtained in **d**), and stir the solution.
- f) Add potassium hydroxide solution (approximately 3 mol/L) of the same amount as **c**), stir, and leave to stand for 2 min to 3 min²¹⁾. Add approximately 0.05 g of calcein indicator or calcein-PPC indicator, and titrate with EDTA standard solution (0.02 mol/L) as similarly to the procedure in **d**)²²⁾.

Notes ²¹⁾ The results obtained when the pH of the solution is outside the range 12.7 to 13.2 can be unreliable.

²²⁾ Judgment of end point can be easier if performed on black paper.

10.2.3.2 Photometric determination of the end-point

- a) Standardize the EDTA standard solution (0.02 mol/L) according to **10.1.3.2 a**).
- b) Perform the procedures in **10.2.3.1 b**) to **e**).

- c) Add potassium hydroxide solution (approximately 3 mol/L) of the same amount as in **10.2.3.1 c)**, stir, and leave to stand for 2 min to 3 min. Add 0.05 g of calcein indicator or calcein-PPC indicator, and while stirring, titrate with the EDTA standard solution (0.02 mol/L) using the apparatus for photometric titration specified in **8.3**, and at each titration volume, measure the absorbance at a wavelength of around 530 nm.
- d) After the colour of the solution turns completely orange (with no fluorescence) in the case of using calcein indicator, or completely reddish violet (with no fluorescence) in the case of using calcein-PPC indicator, perform over-titration by an amount of about 1 ml, and end the measurement ²⁰⁾.
- e) Plot the relation between the volume of titration and the absorbance of the solution. Construct a titration curve, and find an inflection point or the point where the titration curve shows the maximum gradient, and regard its value on the abscissa as the end point ¹⁴⁾.

10.2.4 Calculation

Calculate the calcium oxide content in the sample from the following formula:

$$CaO = \frac{v \times E}{m} \times \frac{250}{20} \times 100$$

where, CaO : calcium oxide content (%)

v : consumed volume of EDTA standard solution (0.02 mol/L), determined in **10.2.3.1 f)** or **10.2.3.2 e)** (ml)

E : amount of calcium oxide equivalent to 1 ml of EDTA standard solution (0.02 mol/L), determined in **10.1.3.1 a)** or **10.1.3.2 a)** (g)

m : mass of sample in **7.3** (g)

10.2.5 Tolerance

The tolerance shall be 0.25 %.

11 Determination of magnesium oxide

11.1 Principle

An aliquot of a certain volume is taken from the sample solution (A) stored after prepared in **7.4 d)**, and the absorbance of magnesium is measured using an atomic absorption spectrometer.

11.2 Reagents

The following reagents shall be used:

- a) **Magnesium oxide standard stock solution (MgO: 1 mg/ml)** Weigh out 0.603 g of metallic magnesium (99.0 % or more), add about 10 ml of hydrochloric acid (1+1) to dissolve, transfer it into a 1 000-ml volumetric flask, make up to the mark with water and shake to mix. Alternatively, dilute a magnesium standard solution which

is traceable to the national measurement standard and available on the market, so as to make it approximately 1 mg/ml in magnesium.

- b) **Magnesium oxide standard solution**¹⁵⁾ Dilute the magnesium oxide standard stock solution five times and take aliquots increased from 0 ml to 10 ml (0 mg to 2.0 mg of MgO) in as many 100-ml volumetric flasks. Add to each of them perchloric acid (1+500) up to the mark and shake to mix.

11.3 Apparatus

An atomic absorption spectrometer shall be used.

11.4 Procedure

Perform the determination according to the following procedures:

- a) Take an aliquot of a certain volume²³⁾ from the sample solution (A) stored after prepared in **7.4 d)** into a 100-ml volumetric flask, make up to the mark with water and shake to mix. This solution is used as test solution (C).
- b) Using a light source lamp for magnesium of the atomic absorption spectrometer, measure the absorbance of the sample solution (C) at the wavelength of 285.2 nm.

The conditions for the apparatus, such as the current in the lamp, slit width of spectrometer, pressure of burning gas or supporting gas, flow rate, and the position of light flux, shall be appropriately established depending on the type of the apparatus. For the shortage of sensitivity, either a scale magnifying device is used or the sensitivity is adjusted by the built-in sensitivity controlling device. When the sensitivity is unnecessarily high, it shall be reduced by adjusting the angle of light flux.

Note ²³⁾ The volume of the aliquot taken here shall depend upon the content of magnesium oxide and the type of the apparatus. Normally, typical amount of 10 ml should be taken.

11.5 Construction of calibration curve

Using a light source for magnesium of the atomic absorption spectrometer, measure each absorbance of the magnesium standard solution at the wavelength of 285.2 nm and construct a calibration curve.

11.6 Calculation

Obtain the amount of magnesium oxide in sample solution (C) from the calibration curve constructed in **11.5**, and calculate the content of magnesium oxide in the sample from the following formula:

$$MgO = \frac{c}{m} \times \frac{250}{v} \times 100$$

where, *MgO* : magnesium oxide content (%)

c : amount of magnesium oxide in sample solution (C)
(g/100 ml)

m : mass of sample in **7.3** (g)

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

11.7 Tolerance

The tolerance shall be 0.15 %.

12 Determination of sulfur trioxide

12.1 Principle

Barium chloride solution is added to either an aliquot of sample solution (F) stored after prepared in **6.4 c)** or the filtrate (including washings) so that the precipitate of barium sulfate is produced. Once the precipitate has been separated by filtering, it is ignited, and its mass is weighed.

12.2 Reagent

The following reagent shall be used:

- a) **Barium chloride solution (100 g/L)** Dissolve 100 g of barium chloride in water to make 1 000 ml.

12.3 Procedure

Perform the determination according to the following procedures:

- a) Take a 200-ml aliquot from the sample solution (F) stored after prepared in **6.4 c)** with a volumetric pipette into a 500-ml beaker.

When the determination of titanium (IV) oxide is not carried out, use all of the filtrate and washings preserved in **6.4 c)** for the determination of sulfur trioxide.

- b) Heat the solution and boil it for 5 min. Maintain the solution at boiling point while agitating the solution carefully, drop gradually 10 ml of barium chloride warm solution (100 g/L) by using a pipette, and furthermore continue to boil it for several minutes.
- c) The solution is left to stand for about 3 h at a near boiling temperature, with cares to maintain the volume of the solution approximately 200 ml, adding warm water, if needed.
- d) Filter the precipitate using a filter paper (Class 6, 110 mm) conforming to **JIS P 3801** and wash with warm water 8 to 10 times.
- e) Dry the precipitate in a crucible, gradually heat to incinerate the filter paper with cares not to allow emission of flame, ignite it for 30 min in an electric furnace maintained at the temperature of $950\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$, allow to cool in desiccator, and weigh the mass.

12.4 Calculation

Calculate the sulfur trioxide content from the following formula:

$$SO_3 = \frac{m' \times 0.343}{m} \times \frac{250}{200} \times 100$$

where, SO_3 : sulfur trioxide content (%)

m : mass of sample in **6.3** (g)

m' : mass of sulfur barium (precipitate) (g)

Where the entire volume of the solution stored after prepared in **6.4 c**) has been used for determination of sulfur trioxide, the content of sulfur trioxide shall be calculated from the following formula:

$$SO_3 = \frac{m' \times 0.343}{m} \times 100$$

where, SO_3 : sulfur trioxide content (%)

m : mass of sample in **6.3** (g)

m' : mass of sulfur barium (precipitate) (g)

12.5 Tolerance

The tolerance shall be 0.10 %.

13 Determination of sodium oxide and potassium oxide

13.1 Atomic absorption spectrometry

13.1.1 Principle

With an aliquot taken from the sample solution (A) stored after prepared in **7.4 d**), the absorbances of sodium oxide and potassium oxide are measured by means of an atomic absorption spectrometer.

13.1.2 Reagents

The following reagents shall be used:

- Calcium stock solution** Add 300 ml of water to 114.3 g of calcium carbonate for alkaline analysis and while stirring, gradually add 600 ml of perchloric acid (60 %) to dissolve. Allow this to cool to the room temperature, and transfer into a 1 000-ml volumetric flask, make up to the mark with water and shake to mix, and store in a polyethylene bottle. One millilitre of this solution contains 64 mg of CaO.
- Sodium chloride (99.5 % or more)** Maintain at a temperature of 500 °C to 650 °C for 45 min to 50 min, and then allow to cool in a sulfuric-acid desiccator.
- Potassium chloride (99.5 % or more)** Maintain at a temperature of 110 °C for 2 to 3 days, and allow to cool in a sulfuric-acid desiccator.
- Alkaline stock solution** Dissolve 1.886 g of sodium chloride and 1.583 g of potassium chloride in an appropriate amount of water, and transfer into a 1 000-ml volumetric flask. Make up to the mark with water, shake to mix and store in a polyethylene bottle. One millilitre of this solution contains 1 mg of Na₂O and K₂O. Alternatively, dilute a sodium standard solution and a potassium standard solution which are traceable to the national measurement standard and available on the market, so as to make it approximately 1 mg/ml in Na₂O and approximately 1 mg/ml in K₂O.

- e) **Alkali oxide mixed stock solution** Prepare this solution according to table 2. Use a volumetric pipette or a burette to take aliquots of the calcium and alkali stock solutions in 1 000-ml volumetric flask, make up to the mark with water and shake to mix. This mixed stock solution shall be stored in a polyethylene bottle.

Table 2 Mixing ratio of alkali oxide mixed stock solution

Classification of alkali oxide mixed stock solution		Mixing ratio	
No.	Amount of alkali in the mixed stock solution (as Na ₂ O, K ₂ O) mg/L	Calcium stock solution ml	Alkaline stock solution ml
No. 1	100	100	100
No. 2	75	100	75
No. 3	50	100	50
No. 4	25	100	25
No. 5	10	100	10
No. 6	0	100	0

- f) **Alkali oxide standard solution** ¹⁵⁾ Dilute accurately 25 times the alkali oxide mixed stock solution.

13.1.3 Apparatus

An atomic absorption spectrometer shall be used.

13.1.4 Procedure

Perform the determination according to the following procedure.

- Take a 10-ml aliquot from the sample solution (A) stored after prepared in 7.4 d) using a volumetric pipette into a 100-ml volumetric flask, make up to the mark with water and shake to mix. Use this solution as sample solution (D).
- Using a light source for sodium of the atomic absorption spectrometer, measure the absorbance of the sample solution (D) at the wavelength of 589.0 nm.
- Using a light source for potassium of the atomic absorption spectrometer, measure the absorbance of the sample solution (D) at the wavelength of 766.5 nm.

13.1.5 Construction of calibration curve

Using a light source for sodium and potassium of the atomic absorption spectrometer, measure each absorbance of the alkali oxide standard solution at the wavelengths of 589.0 nm and 766.5 nm and construct a calibration curve.

The conditions for the apparatus, such as the current in the lamp, slit width of spectrometer, pressure of burning gas and supporting gas, flow rate, and the position of light flux, shall be appropriately established depending on the type of the apparatus used. For the shortage of sensitivity, either a scale magnifying device is used or the sensitivity is adjusted by the built-in sensitivity controlling device. When the sensitivity is unnecessarily high, it shall be reduced by adjusting the angle of light flux.

13.1.6 Calculation

Determine the amount of sodium oxide and potassium oxide in the sample solution (D) from the calibration curve constructed according to **13.1.5**, and calculate the content of the sodium oxide and potassium oxide in the sample from the following formula:

$$Na_2O \text{ or } K_2O = \frac{c}{m} \times \frac{250}{v} \times 100$$

where, Na_2O or K_2O : sodium oxide or potassium oxide content (%)

c : amount of sodium oxide or potassium oxide in sample solution (D) (g/100 ml)

m : mass of sample in **7.3** (g)

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

13.1.7 Tolerance

The tolerance for sodium oxide shall be 0.03 %.

The tolerance for potassium oxide shall be 0.04 %.

13.2 Flame photometry**13.2.1 Principle**

Sample is treated with hydrochloric acid. The contents of sodium oxide and potassium oxide in solutions are determined by means of flame photometry.

This method is specified for cements whose undissolved residue amount does not exceed 3 %.

13.2.2 Reagents

The following reagents shall be used:

- a) **Hydrochloric acid (1+9)**
- b) **Buffer solution** Dissolve 50 g of cesium chloride and 250 g of aluminium nitrate enneahydrate to make about 1 L with water. Prepare this solution immediately before use.
- c) **Sodium chloride (99.5 % or more)** Maintain at a temperature of 500 °C to 650 °C for 40 min to 50 min, and then allow to cool in a sulfuric-acid desiccator.
- d) **Potassium chloride (99.5 % or more)** Maintain at a temperature of 110 °C for 2 to 3 days, and allow to cool in a sulfuric-acid desiccator.
- e) **Alkali preservation solution** ²⁴⁾ Dissolve 0.254 2 g ± 0.000 5 g of sodium chloride and 0.190 7 g ± 0.000 5 g of potassium chloride in water and make constant volume in a 1 000-ml volumetric flask.

Note ²⁴⁾ This solution has a Na concentration of 100 mg/L and K concentration of 100 mg/L.

13.2.3 Apparatus

A flame photometer which is sufficiently stable, and capable of measuring the emission intensities for sodium at 589 nm and potassium at 768 nm shall be used.

13.2.4 Procedure

Perform the determination according to the following procedure:

- Weigh, to the nearest 0.000 1 g, approximately 0.2 g²⁵⁾ of cement into a platinum dish or a porcelain evaporating dish, make into a slurry with 3 ml of water and evaporate to dryness after adding 20 ml of hydrochloric acid (1+9).
- Add hot water and 2 ml of hydrochloric acid (1+9) to the residue, and filter through the filter paper (Class 5 B, 110 mm) conforming to **JIS P 3801**.

The filtrate shall be received in a 100-ml volumetric flask that already contains 10 ml of the buffer solution.

- Wash the residue with hot water until the volumetric flask is almost filled to the mark. Then cool to the room temperature, then make up to the mark with water and shake to mix.
- Measure the emission intensities of the sample solution by a flame photometer, and determine the content (%) of Na₂O and K₂O by reading the scale values in conjunction with the calibration curve in **13.2.5**.

Note ²⁵⁾ In the corresponding International Standard, the sampling range is specified to be 0.200 g ± 0.005 g.

13.2.5 Construction of calibration curve

Whenever a new batch of any reagent is used, determine the alkali content by means of this method.

If the alkali content (calculated according to **13.2.6** with the sample amount being 0.2 g) of a reagent exceeds 0.01 %, either replace the batch with a new one, which shall be verified in the same way or prepare new calibration solutions.

For preparing sample solutions for each point of the calibration curve, evaporate 20 ml of hydrochloric acid (1+9) to dryness. Dissolve the residue with 2 ml of hydrochloric acid (1+9) and 3 ml of water. Transfer the solution into a 100-ml volumetric flask, and add 10 ml of buffer solution. After adding the quantities of the alkali preservation solution shown in table 3 to the individual volumetric flasks using a burette, add water to the mark and shake to mix.

Table 3 Quantities of preservation solution added to the flasks

Volumetric flask No.	1	2	3	4	5	6	7
Preservation solution mL	0	1	3	5	10	20	30

The alkali contents of flasks 1 to 7 shall be the values converted to the content rate (%) of sodium oxide or potassium oxide in the cement, with the sample amount being 0.200 0 g. These values are shown in table 4.

Table 4 Alkali contents of preservation solutions in flasks

Volumetric flask No.	1	2	3	4	5	6	7
Na ₂ O %	0	0.07	0.20	0.34	0.67	1.35	2.02
K ₂ O %	0	0.06	0.18	0.30	0.60	1.20	1.80

Aspirate the calibration solutions into the flame of the flame photometer. Aspirate the blank solution in flask 1 first and set the indication on the apparatus to zero.

Then aspirate the other calibration solutions in order of increasing alkali content (in flasks 2 to 7). Measure the intensities for Na₂O at 589 nm and for K₂O at 768 nm. Construct curves of the measured intensities against the corresponding contents of sodium oxide and potassium oxide in the calibration solutions.

13.2.6 Calculation

Obtain the temporary content (%) of sodium oxide and potassium oxide in the case of 0.200 0 g sample amount from the calibration curve constructed in 13.2.5, and correct the content of sodium oxide and potassium oxide in sample from the following formula:

$$Na_2O \text{ or } K_2O = \frac{c}{m} \times 0.2000$$

where, Na_2O or K_2O : sodium oxide or potassium oxide content (%)

c : temporary content of sodium oxide or potassium oxide (%)

m : mass of sample in 13.2.4 a) (g)

13.2.7 Tolerance

The tolerance for sodium oxide shall be 0.03 %.

The tolerance for potassium oxide shall be 0.04 %.

14 Determination of titanium (IV) oxide

14.1 Principle

An aliquot of the sample solution (F) stored after prepared in 6.4 c) shall be taken, and after its hydrochloric acid concentration is regulated, iron is reduced with addition of ascorbic acid. Then add diantipyrimethane solution to colour the sample solution and measure the absorbance.

14.2 Reagents

The following reagents shall be used:

- Ascorbic acid solution (100 g/L)** This solution shall be stored in a polyethylene bottle and placed in a dark and cold place²⁶⁾.
- Diantipyrimethane solution (20 g/L)** Dissolve 2 g of diantipyrimethane in 30 ml of hydrochloric acid (1+5), and make a total of 100 ml with water.
- Titanium (IV) oxide standard stock solution (TiO₂: 0.20 mg/ml)** Take titanium (IV) oxide (99.0 % or more) in a crucible, ignite it at about 1 000 °C for 1 h and allow it to cool in a desiccator²⁷⁾. Weigh out 0.200 g of this into a platinum crucible, add 4 g of potassium pyrosulfate, and fuse it. After cooling it, place the platinum crucible in a beaker, add sulfuric acid (1+9), warm it, and dissolve it at 50 °C or lower. Take out the platinum crucible, and after washing with water, transfer the solution into a 1 000-ml volumetric flask, and make up to the mark with sulfuric acid (1+9), and shake to mix. Alternatively, dilute with water a

titanium standard solution available on the market, and prepare so as to make it approximately 0.2 mg/ml in TiO_2 .

- d) **Titanium (IV) oxide standard solution (TiO_2 : 0.01 mg/ml)** Dilute this stock solution 20 times with water immediately before each use.

Notes ²⁶⁾ Solution after 1 month elapse should not be used.

²⁷⁾ This procedure is necessary because titanium oxide (IV) can contain water.

14.3 Procedure

Perform the determination according to the following procedure:

- a) Take an aliquot ²⁸⁾ of the sample solution (F) stored after prepared in **6.4 c)** into a 50-ml volumetric flask, add 5 ml of hydrochloric acid (1+1) and 3 ml of ascorbic acid solution (100 g/L), and after leaving to stand for 1 min, add 20 ml of diantipyril-methane solution (20 g/L), make up to the mark with water, shake to mix and leave to stand for 1 h.
- b) Take an aliquot of the solution into a 10-ml absorption cell, and measure the absorbance, against water, at a wavelength of around 390 nm using the absorption photometer.

Note ²⁸⁾ The volume of aliquot taken here shall depend upon the content of titanium (IV) oxide. The appropriate amount when the content of titanium (IV) oxide is less than 0.5 % is 10 ml.

14.4 Construction of calibration curve

Take aliquots, increased stepwise from 0 ml to 20.0 ml (0 g to 0.200 g as TiO_2), of titanium (IV) oxide standard solution into as many 50-ml volumetric flasks, and perform the procedure in **14.3 a)** and **b)** on each of them and construct a calibration curve.

14.5 Calculation

Determine the amount of titanium (IV) oxide in the coloured solution from the calibration curve constructed in **14.4**, and calculate the content of titanium (IV) oxide in the sample from the following formula:

$$\text{TiO}_2 = \frac{a}{m} \times \frac{250}{v} \times 100$$

where, TiO_2 : titanium (IV) oxide content (%)

a : amount of titanium (IV) oxide in coloured solution (g/50 ml)

m : mass of sample in **6.3** (g)

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

14.6 Tolerance

The tolerance shall be 0.02 %.