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(TARJ/JSA)

**Methods for X-ray fluorescence
spectrometric analysis of refractory
products**

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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 The Technical Association of Refractories, Japan (TARJ)/Japanese Standards Association (JSA) 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 2216 : 1995** is replaced with this Standard.

This revision has been made based on **ISO 12677 : 2003** *Chemical analysis of refractory products by XRF—Fused cast bead method* for the purpose of making it easier to compare this Standard with International Standard; to prepare Japanese Industrial Standard conforming with International Standard; and to propose a draft of an International Standard which is based on Japanese Industrial Standard.

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.

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

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Contents

	Page
Introduction	1
1 Scope	1
2 Normative references	1
3 General matters	2
4 Definitions	2
5 Analysis items	4
6 Determination limit	4
7 Samples	5
7.1 Sampling and preparation	5
7.2 Method of weighing samples	5
8 Determination method	5
8.1 Principle	5
8.2 Reagents, reference materials, and powdered samples for drift correction	6
8.3 Apparatus and instrument	6
8.4 Determination operation	7
9 Record method	14
9.1 Arrangement of analytical values	14
9.2 Test report	15
10 Evaluation method of measurement condition	15
10.1 Evaluation time	15
10.2 Types of evaluation method of measurement condition	15
10.3 Evaluation of glass bead mass	15
10.4 Evaluation of setting condition of X-ray fluorescence spectrometric analysis apparatus	16
Annex 1 (normative) Conditions to be satisfied by refractory series reference materials	20
Annex 2 (normative) Refractory series reference materials	23
Annex 3 (normative) Method of interference correction used to compensate for the effects of co-existing components	30
Annex 4 (normative) Extension method for determination limit of calibration curve using series reference materials	45

Annex 5 (informative)	Calculation method of theoretical mass absorption correction coefficient	49
Annex 6 (informative)	Multiple regression method which does not use binary system calibration curve	52
Annex 7 (informative)	Practical examples of interference correction used to compensate for the effects of coexisting components of chromium-magnesia refractory	54
Annex 8 (informative)	Preparation method of sample synthesized from reagent and guideline on evaluation method by sample synthesized from reagent	62
Annex 9 (informative)	Preparation method of glass bead for calibration curve by reagent blending	69
Annex 10 (informative)	Comparison table between JIS and corresponding International Standard	73

Methods for X-ray fluorescence spectrometric analysis of refractory products

Introduction This Japanese Industrial Standard has been prepared based on the first edition of **ISO 12677** *Chemical analysis of refractory products by XRF—Fused cast bead method* published in 2003 with some modifications of the technical contents.

The portions given sidelines or dotted underlines are the matters modified from the original International Standard. A list of modifications with the explanations is given in Annex 10 (informative).

1 Scope This Standard specifies methods for X-ray fluorescence spectrometric analysis of oxides in refractory products and materials by means of the glass bead method.

Remarks : The International Standard corresponding to this Standard is as follows.

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

ISO 12677:2003 *Chemical analysis of refractory products by XRF—Fused cast bead method* (MOD)

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 *General rules for chemical analysis*

JIS K 0119 *General rules for X-ray fluorescence spectrometric analysis*

JIS K 0211 *Technical terms for analytical chemistry (General part)*

JIS K 0215 *Technical terms for analytical chemistry (Analytical instrument part)*

JIS Q 0034 *General requirements for the competence of reference material producer*

JIS Q 0035 *Certification of reference materials—General and statistical principles*

JIS R 1301 *Porcelain crucibles for chemical analysis*

JIS R 2012 *Methods for chemical analysis of refractories containing zircon and/or zirconia*

JIS R 2013 *Methods for chemical analysis of refractories containing alumina, zirconia and silica*

- JIS R 2014 *Methods for chemical analysis of refractories containing alumina and magnesia*
- JIS R 2212-1 *Methods for chemical analysis of refractory products—Part 1: Fire-clay refractories (to be established)*
- JIS R 2212-2 *Methods for chemical analysis of refractory products—Part 2: Silica refractories (to be established)*
- JIS R 2212-3 *Methods for chemical analysis of refractory products—Part 3: High alumina refractories (to be established)*
- JIS R 2212-4 *Methods for chemical analysis of refractory products—Part 4: Magnesite and/or dolomite refractories (to be established)*
- JIS R 2212-5 *Methods for chemical analysis of refractory products—Part 5: Chrome-magnesia refractories (to be established)*
- JIS Z 8401 *Guide to the rounding of numbers*
- JIS Z 8801-1 *Test sieves—Part 1: Test sieves of metal wire cloth*
- ISO/IEC Directives:1992 part 2 *Methodology for the development of International Standards—Annex B Mention of reference materials*

3 General matters The general matters of the analysis method shall be as specified in **JIS K 0050** and **JIS K 0119**. The general matters of a sieve shall be as specified in **JIS Z 8801-1**.

4 Definitions For the purpose of this Standard, the definitions given in **JIS K 0119**, **JIS K 0211** and **JIS K 0215**, and the following definitions apply.

a) **powdered sample** a powdered sample used for preparing a glass bead by adding a flux

It is classified into a reference material, a powdered sample for drift correction, a powdered sample for analysis, and a sample synthesized from reagent.

1) **reference material** a series of sample of which the composition is known used for the creation of a calibration curve, the evaluation of measurement condition and tolerance

It is classified into the following two types.

1.1) **refractory series reference materials** a series of reference material groups of which the composition is suitably prepared in order to use for the X-ray fluorescence spectrometric analysis of refractory

1.2) **supplementary reference materials** reference materials used in order to supplement refractory series reference materials

2) **powdered sample for drift correction** a powdered sample used for preparation of drift-corrected beads

3) **powdered sample for analysis** a powdered sample obtained by grinding ignition residues of a sample for analysis

- 4) **sample synthesized from reagent** sample powder of which the composition values are known, which is prepared by weighing out high-purity reagents of fine powder correctly

It is used for the evaluation of the accuracy of the calibration curve in Annex 8, the preparing accuracy of glass beads and the tolerance of reproducibility of apparatus.

- b) **glass bead** a circular vitrified melt product with a flat surface prepared from a powdered sample in order to use for X-ray fluorescence spectrometric analysis

It is classified into a bead for calibration curve, a bead for drift correction, a bead for evaluation, a sample bead for reagent synthesis and an analysis bead.

- 1) **bead for calibration curve** a glass bead used for creating a calibration curve and a formula of interference correction used to compensate for the effects of coexisting components
- 2) **bead for drift correction** a glass bead used in order to convert into the condition at the time of creation of a calibration curve and a formula of interference correction used to compensate for the effects of coexisting components by confirming variation with time of X-ray fluorescence intensity (hereinafter referred to as "X-ray intensity") under the predetermined operational condition of apparatus
- 3) **bead for evaluation** a glass bead used for the evaluation of the measurement condition and analysis accuracy

It is classified into the following two types.

- 3.1) **bead for evaluation of measurement condition** a glass bead used for the evaluation of the glass bead preparation condition and the analysis condition of X-ray fluorescence spectrometric analysis apparatus
 - 3.2) **bead for checking the analysis tolerance** a glass bead used in order to evaluation whether analysis accuracy is ensured for routine analysis
 - 4) **bead of sample synthesized from reagent** a glass bead used for the evaluation specified in Annex 8, which is prepared from a sample synthesized from reagent
 - 5) **analysis bead** a glass bead prepared with a powdered sample for analysis
- c) **reference X-ray intensity** X-ray intensity which is taken as the reference for converting into the condition of X-ray intensity at the time of creation of a calibration curve and a formula of interference correction used to compensate for the effects of coexisting components

In general, it is the X-ray intensity of beads for drift correction measured in parallel to beads for calibration curve or the value obtained by multiplying the X-ray intensity by a fixed value.

- d) **drift-corrected X-ray intensity** the value obtained by converting the measured X-ray intensity so that a calibration curve and a formula of interference correction used to compensate for the effects of coexisting components can be used under the predetermined operational conditions of apparatus

5 Analysis items The analysis items specified this Standard shall be as follows.

- a) Loss on ignition (LOI)
- b) Silicon (IV) oxide (SiO_2)
- c) Aluminium oxide (Al_2O_3)
- d) Iron (III) oxide (all iron) (Fe_2O_3)
- e) Titanium (IV) oxide (TiO_2)
- f) Manganese (II) oxide (MnO)
- g) Calcium oxide (CaO)
- h) Magnesium oxide (MgO)
- i) Sodium oxide (Na_2O)
- j) Potassium oxide (K_2O)
- k) Chromium (III) oxide (Cr_2O_3)
- l) Zirconium oxide (ZrO_2)
- m) Phosphorus (V) oxide (P_2O_5)
- n) Hafnium oxide (HfO_2)

6 Determination limit The determination limit of this Standard shall be as specified in table 1. However, this value shall be a value in the sample after the measurement of loss on ignition.

Table 1 Determination limit

Unit : % (mass fraction)

	Material division of refractory products							
	Argillaceous	Quartzite	High-alumina	Magnesia	CM	ZS	AZS	AM
SiO_2	40 to 90	85 to 98	0.1 to 45	0.1 to 8	1 to 10	0.01 to 45	0.01 to 45	0.1 to 5
Al_2O_3	10 to 45	0.1 to 10	40 to 95	0.5 to 8	2 to 30	0.01 to 7	10 to 80	10 to 95
Fe_2O_3	0.3 to 4	0.02 to 4	0.01 to 4	0.05 to 3	0.5 to 25	0.01 to 3	0.01 to 2	0.3 to 5
TiO_2	0.3 to 3	0.01 to 0.2	0.01 to 5	—	0.01 to 1	0.01 to 2	0.01 to 5	0.01 to 3
MnO	0.01 to 0.2	0.01 to 0.2	0.01 to 0.2	—	0.01 to 0.2	—	—	—
CaO	0.01 to 1	0.01 to 4	0.01 to 1	0.01 to 5	0.01 to 5	0.01 to 6	0.01 to 2	0.01 to 5
MgO	0.01 to 1	0.01 to 0.2	0.01 to 1	80 to 99	15 to 85	0.01 to 5	0.01 to 2	3 to 80
Na_2O	0.01 to 3	0.01 to 0.5	0.01 to 1	—	—	0.01 to 2	0.01 to 3	0.01 to 3
K_2O	0.01 to 3	0.01 to 0.5	0.01 to 3	—	—	0.01 to 2	0.01 to 1	0.01 to 1
Cr_2O_3	0.01 to 1	—	—	—	2 to 50	0.01 to 3	—	—
ZrO_2	0.01 to 1	—	—	—	—	45 to 96	5 to 50	—
P_2O_5	0.01 to 1	—	—	—	—	0.01 to 2	—	0.01 to 1
HfO_2	—	—	—	—	—	0.05 to 2	0.05 to 2	—

Remarks : CM: chromium-magnesia, ZS: zircon-zirconia,
AZS: alumina-zirconia-silica, AM: alumina-magnesia.

7 Samples

7.1 Sampling and preparation The sampling and preparation shall be as follows.

- a) For the refractory brick and raw material, take the sample of quantity designated in accordance with the agreement between the purchaser and the manufacturer at random from a lot. Grind the whole quantity of the sample taken, sieve the ground powder through a sieve of 6.7 mm aperture specified in **JIS Z 8801-1**, reduce until it becomes about 100 g using a riffle sampler or a method of quartering, and grind the whole quantity until it passes through a sieve of 300 μm aperture specified in **JIS Z 8801-1**.
- b) Divide the unshaped refractory into the dry condition and the wet condition according to its properties, and prepare about 100 g of laboratory samples as follows.
 - 1) **In the case of dry unshaped refractory** Sample one bag or 50 kg at random from a lot, reduce until it becomes about 100 g using a riffle sampler or a method of quartering, and grind the whole quantity until it passes through a sieve of 300 μm aperture specified in **JIS Z 8801-1**.
 - 2) **In the case of wet unshaped refractory** Sample the whole quantity of one container at random from a lot, and mix sufficiently in the sample container or in the clean container which does not react with the unshaped refractory with a clean stirrer, etc. until it becomes uniform. Take about 100 g of this whole quantity on the heat-resistant plate (for example, tetrafluoroethylene resin plate) which does not react with mortar, spread it out in a shape of a thin disk so that the thickness becomes 10 mm or less, and dry it in an air bath of 110 ± 5 °C for 10 h or longer. Grind this whole quantity until it passes through a sieve of 300 μm aperture specified in **JIS Z 8801-1**.
- c) Reduce the laboratory sample obtained in a) and b) until it becomes about 10 g using a method of quartering. Grind this finely to such a degree that it completely passes through a sieve of 106 μm aperture specified in **JIS Z 8801-1**, spread it out thinly in a flat weighing bottle (50 mm $\times$ 30 mm), and after making it dry in an air bath of 110 ± 5 °C for 2 h or longer, allow it to cool in a desiccator to store. Take this as the sample for chemical analysis.

7.2 Method of weighing samples For weighing out analysis samples, measure the specified quantity to the nearest 0.1 mg correctly using a chemical balance.

8 Determination method

8.1 Principle The powdered sample is fused with a suitable flux to destroy its mineralogical and particulate composition. The resultant melt is cast into the shape of a glass bead which is then introduced into an XRF spectrometer. The intensities of the fluorescent X-rays of the required elements in the bead are measured and the chemical composition of the sample is analysed by reference to previously determined calibration graphs or formulae and applying corrections for inter-element effects.

8.2 Reagents, reference materials, and powdered samples for drift correction The reagents, reference materials, powdered samples for drift correction shall use the following.

- a) **Flux** Put lithium tetraborate (anhydrous) ⁽¹⁾ into a platinum dish (for example, No. 150), and after drying it at 650 °C to 700 °C for about 4 h in an electric furnace, cool it in a desiccator to store.

Note ⁽¹⁾ Use high-purity lithium tetraborate with a low blank test value. The content of the component to be determined contained in the reagent should be not more than 0.001 % (mass fraction). Since a blank test value fluctuates when a lot changes and it may have effects on the determined value, the reagent of the same lot should be secured as much as possible. If a lot changes, perform the determination of several beads for checking the analysis tolerance or several beads for calibration curve, and when it exceeds the permissible error, re-create the calibration curve using new fluxes.

- b) **Release accelerator** After dissolving 25 g of lithium iodide (dihydrate) in water to make 50 ml, put it into a plastic container to store.

- c) **Oxidizing agent** Use lithium nitrate (anhydrous). Store it in a desiccator.

- d) **Reference materials**

- 1) **Refractory series reference materials** The refractory series reference materials used in this Standard shall be prepared for each measurement material as given in Annex 1, and the composition shall be clarified. The refractory series reference materials shall be given in Annex 2.

- 2) **Supplementary reference materials** For the purpose of supplementing refractory series reference materials, use the sample of which the content is correctly determined in accordance with the chemical analysis method specified in Japanese Industrial Standard or the chemical analysis method which conforms to this. Use for the extension of determination limit in Annex 4.

- e) **Powdered sample for drift correction** Use the material which is homogeneous and hard to deteriorate. Use the material which adapts to the component to be determined, such as the high-purity material of which the main component is the component to be determined, the material of which the composition of analysis sample is similar, the material which contains multiple impurities to be determined of a fixed quantity.

8.3 Apparatus and instrument The apparatus and instrument shall be as follows.

- a) **X-ray fluorescence spectrometric analysis apparatus** The wavelength-dispersive X-ray fluorescence spectrometric analysis apparatus specified in **JIS K 0119** shall be used. The apparatus to be used shall have a sufficient sensitivity of measurement in a range up to 0.01 % (mass fraction) of the content of each component and satisfy the detection limit and repeatability sufficiently when the evaluation is performed in accordance with clause 10. In order to obtain the sensibility of light element components, the X-ray tube which uses rhodium or chromium as anticathode should be used.

- b) **Glass bead preparation apparatus** The electric resistance furnace or high frequency induction furnace which can be heated up to a fixed temperature between 1 100 °C and 1 250 °C to prepare glass bead shall be used. In order to obtain a glass bead without component segregation and blowhole, the automatic fusion apparatus shall have a mechanism for stirring the fusion. Furthermore, the structure of the apparatus by which a glass bead is manually prepared shall be such that the fusion can be easily stirred in the furnace.
- c) **Glass bead preparation container** The glass bead preparation container of which the structure is hard to deform by the heat fusion operation with the internal bottom face made of platinum alloy ⁽²⁾ finished smoothly. The internal bottom face of the container shall be always kept smooth. The example of the glass bead preparation container is shown in figure 1.

Note ⁽²⁾ For the material of the container, for example, platinum [95 % (mass fraction)] – gold [5 % (mass fraction)] shall be used.

Unit : mm

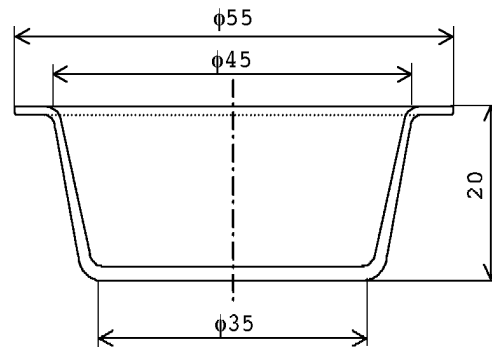


Figure 1 Example of glass bead preparation container

8.4 Determination operation

8.4.1 **Measurement of loss on ignition** The determination of loss on ignition shall be as follows.

- a) **Read of crucible mass** Heat a platinum crucible (for example, with a No. 30 cover) or a porcelain crucible PC1B15 ml specified in **JIS R 1301** at 1 050 ± 25 °C, and after allowing it to cool in a desiccator, measure its mass. Repeat this operation until it becomes constant mass ⁽³⁾.

Note ⁽³⁾ The point when the difference in mass between before and after the operation of repetition becomes 0.3 mg or less is taken as the constant mass. Through the determination operation of loss on ignition, the blank test value to be obtained by performing the operations of **a)** and **b)** in parallel using the empty crucible in place of the crucible into which the sample is put may be prepared for the measurement of fluctuation of the measurement condition (ignition, chemical balance, indoor environment).

- b) **Read of mass of crucible and sample** Weigh out about 1.00 g of analysis sample prepared in 7.1 c) into the crucible which became constant mass, and read the mass of the whole crucible correctly to the nearest 0.1 mg.

- c) **Read of mass after ignition** Without covering the crucible, first, heat at low temperature, gradually raise temperature, finally, heat at $1\,050\text{ }^{\circ}\text{C} \pm 25\text{ }^{\circ}\text{C}$ for about 60 min in the electric furnace, and cover the crucible, after allowing it to cool in a desiccator, measure its mass. Repeat this operation until it becomes constant mass ⁽³⁾.
- d) **Calculation of loss on ignition and powdered sample for analysis** Calculate ⁽⁴⁾ the loss on ignition according to the following formula. If sintering is detected in the residue after the measurement of loss on ignition, grind lightly, store it in a desiccator, and use it as the powdered sample for analysis in **8.4.2 a)**.

$$LOI = \frac{m_1 - m_2}{m_1 - m_0} \times 100$$

where, LOI : Loss on ignition [% (mass fraction)]

m_0 : Mass obtained in **8.4.1 a)** (g)

m_1 : Mass obtained in **8.4.1 b)** (g)

m_2 : Mass obtained in **8.4.1 c)** (g)

Note ⁽⁴⁾ When mass increases, “-” (minus sign) is attached before a percentage.

8.4.2 Weighing out of powdered samples for analysis, fluxes, and oxidizing agents The weighing out of the powdered samples for analysis, fluxes, and oxidizing agents shall be performed as follows.

- a) **Weighing out of powdered samples for analysis** Weigh out a fixed quantity (in general, 0.300 0 g; in the case of chromium-magnesia, 0.200 0 g) from the powdered samples for analysis obtained in **8.4.1 d)** using a chemical balance correctly to the nearest 0.1 mg.
- b) **Weighing out of fluxes** Weigh out a fixed multiple quantity of powdered samples for analysis (in general, 3.000 0 g of 10 times the quantity; in the case of chromium-magnesia, 4.000 0 g of 20 times the quantity) of fluxes in **8.2 a)** using a chemical balance correctly to the nearest 0.1 mg.
- c) **Weighing out of oxidizing agents** For the chromium-magnesia samples, weigh out fixed multiple quantity of powdered samples for analysis (in general, 2.000 0 g of 10 times the quantity) of oxidizing agent in **8.2 c)** using a chemical balance correctly to the nearest 0.1 mg.

8.4.3 Preparation of analysis beads and beads for checking the analysis tolerance The preparation of analysis beads and beads for checking the analysis tolerance ⁽⁵⁾ shall be performed as follows.

Note ⁽⁵⁾ Select the reference material of which the chemical composition is near that of the analysis sample, weigh out the sample in accordance with **8.4.2 a)**, perform the next preparation of analysis bead in parallel, and use for evaluation of analysis tolerance in **8.4.5**.

- a) Before moving or after moving the powdered sample for analysis and flux weighed out into the glass bead preparation container in **8.3 c)**, mix sufficiently, add a fixed quantity (about 50 μl) ⁽⁶⁾ of release accelerator in **8.2 b)** to this, and if necessary, heat at low temperature and evaporate moisture. In the case of chromium magnesia, add the oxidizing agent in **8.4.2 c)** to this, and mix it.

Note ⁽⁶⁾ The addition quantity should be changed according to material. However, the quantity consumed of the bead for calibration curve, the bead for drift correction, the bead for evaluation, and the analysis bead of each material shall be unified and fixed. In place of the release accelerator, release properties may be made to improve by spraying coolant gas when the glass bead in **8.4.3 c)** is allowed to cool. In this case, the addition of release accelerator is unnecessary.

- b) Carry out the fusion at 1 100 °C to 1 200 °C ⁽⁷⁾ for a fixed time (about 10 min) ⁽⁸⁾, during this time, sometimes shake the glass bead preparation container, and make blowhole emit as well as homogenize the fused.

Information : For the apparatus using the high-frequency induction furnace, if the glass bead preparation container is covered with a platinum cover, the fusion will become easy to carry out.

Notes ⁽⁷⁾ For the chromium-magnesia sample, the fusion temperature should be made to be 1 200 °C to 1 250 °C.

- ⁽⁸⁾ In order to avoid vaporization of flux, it is necessary to make the fusion temperature and fusion time exact. The fusion condition such as fusion temperature, fusion time shall be determined in accordance with the evaluation in clause 10. If the homogeneous glass bead can be prepared, the fusion temperature should be low and the fusion time should be controlled to be short.

However, even the transparent glass bead on an appearance may be heterogeneous. Care shall be taken since, when it is heterogeneous, especially the surface layer remarkably reduces the analysis accuracy of the light element oxides lighter than silicon dioxide which become the analysis target.

- c) After the completion of fusion, allow it to cool, take out the glass bead, and take the side which is in contact with the bottom face of glass bead preparation container as the X-ray irradiation surface.

8.4.4 Creation of calibration curve The creation of the calibration curve shall be as follows.

- a) **Preparation of the bead for calibration curve** Use each reference material of the refractory series reference materials in Annex 2 in place of the powdered samples for analysis, perform the operations in **8.4.3 a)** to **c)**, and prepare the bead for calibration curve of ten or more kinds for each material ⁽⁹⁾.

Notes ⁽⁹⁾ While the calibration curve in **8.4.4 d)** can be made to interpolate the determination limit in table 1 of clause 6, in order to complete the calibration curve, not only the supplementary reference material ⁽¹⁰⁾ in **8.2 d) 2)** can be used, but also the refractory reference material of the same material, the refractory reference material and the supplementary reference material ⁽¹⁰⁾, or the refractory reference material of other materials can be used taking the glass bead prepared by weighing correctly with a chemical balance so that the quantity weighed out in **8.4.2 a)** is obtained as the bead for calibration curve.

- ⁽¹⁰⁾ A high-purity reagent can be used. Furthermore, the method in which the solution obtained by dissolving high-purity metal with nitric acid, etc. is added correctly, etc. can also be used.

- b) **Preparation of bead for drift correction** Use the powdered sample for drift correction in place of the powdered sample for analysis, perform the operations in **8.4.3 a) to c)**, and prepare several kinds of the bead for drift correction for each material ⁽¹¹⁾.

Note ⁽¹¹⁾ Since the bead for drift correction is used to reproduce the condition of X-ray intensity at the time of creation of the calibration curve, the powdered sample for drift correction which can be stably supplied over a long period of time shall be used. Furthermore, for the bead for drift correction, the first bead for drift correction and the second bead for drift correction shall be provided for each analytical component for each material. Since the first bead for drift correction is selected from the bead for drift correction of the highest content for each analytical component, and the second bead for drift correction is selected from the bead for drift correction in which the component is hardly contained for each analytical component, it is necessary to devise so that the whole analytical components can be covered by the minimum bead for drift correction for each material.

- c) **Measurement of X-ray fluorescence intensity of bead for calibration curve and bead for drift correction and performing of drift correction** Perform the measurement according to the X-ray fluorescence analysis condition which was set by evaluating the bead for calibration curve and bead for drift correction in clause **10**, obtain the X-ray intensity of each analytical component, and perform the drift correction of the measured values ⁽¹²⁾.

Note ⁽¹²⁾ The general formula for drift correction shall be as given in the following formulae (1) to (3).

$$I = \alpha I' + \beta \dots\dots\dots (1)$$

$$\alpha = \frac{R}{N_{s1} - N_{s2}} \dots\dots\dots (2)$$

$$\beta = \frac{-R \times N_{s2}}{N_{s1} - N_{s2}} \dots\dots\dots (3)$$

where,

I : Drift-corrected X-ray intensity of bead for calibration curve and bead for drift correction

I' : X-ray intensity of bead for calibration curve and bead for drift correction (count)

N_{s1} : X-ray intensity of the first bead for drift correction (count)

N_{s2} : X-ray intensity of the second bead for drift correction (count)

α : Correction coefficient (gradient coefficient)

β : Correction coefficient (intercept coefficient)

R : Constant

For example, when the intensity ratio method which sets the first bead for drift correction to be 1, and sets the second bead for drift correction to be 0, R becomes 1 and the formula (1) can be arranged and expressed as $I = (I' - N_{s2}) / (N_{s1} - N_{s2})$. Furthermore, when the measured X-ray intensity here is taken as the drift-corrected X-ray intensity, the formula (1) can be arranged and expressed as $I = I'$. Except for when the intensity ratio method is used, the X-ray intensity of the first bead for drift correction and the second bead for drift correction at this time shall be stored and used for calculation of drift correction in the formula (6) and the formula (7) of 8.4.5.

- d) **Preparation of calibration curve** Obtain a relation formula (4) of the components and drift-corrected X-ray intensities of the beads used for the calibration curve calculated in 8.4.4 c) by means of the method specified in Annex 3 to obtain the calibration curve ⁽¹³⁾.

$$W_i = (aI_i^2 + bI_i + c)(1 + \sum d_j W_j) + \sum l_j W_j \dots\dots\dots (4)$$

where, W_i : the corrected content of component i
[% (mass fraction)]
 I_i : the drift-corrected X-ray intensity of component i
 d_j : the matrix correction coefficient of coexisting component j
 W_j : the content of coexisting element j [% mass fraction]
 l_j : the over-lapping correction coefficient of coexisting component j
 a, b, c : the coefficients

Note ⁽¹³⁾ Formula (4) is called a coexisting component correction formula. This formula can be easily obtained by an X-ray fluorescence spectrometer equipped with a computer. Calibration curves for light-element oxides can be obtained, in accordance with the least squares method, by simple quadratic or linear regression formula without correction terms, $W_i = aI_i^2 + bI_i + c$ or $W_i = bl_i + c$, which are expressed by $(I + \sum d_j W_j) + \sum l_j W_j$. Which calibration formula is the most suitable can be determined by verifying the accuracy of the calibration curve by formula (5) and seeing if the accuracy is improved.

In many cases, this accuracy can be obtained together with the calculation of the calibration curves by the computer attached to the X-ray fluorescence spectrometer.

$$\sigma_i = \sqrt{\frac{\sum (W_i - W'_i)^2}{n - \phi}} \dots\dots\dots (5)$$

where, σ_i : the accuracy of component i
 n : the number of beads used for the calibration curve
 ϕ : the number of coefficients obtained (linear formula = 2, quadratic formula = 3)
 W_i : the certified value of component i [% (mass fraction)]
 W'_i : the content of component i from calibration curve as a percentage [% (mass fraction)]

8.4.5 Measurement of analysis bead and bead for checking the analysis tolerance and calculation of analytical value The measurement of the analysis bead and the bead for checking the analysis tolerance and the calculation of analytical values shall be as follows.

- a) **Measurement of X-ray intensity** The analysis bead and the bead for checking the analysis tolerance obtained in **8.4.3 c)** as well as the bead for drift correction shall be measured according to the X-ray fluorescence analysis condition which was set by performing the evaluation in clause **10** in accordance with **8.4.4 c)**.
- b) **Calculation of α and β** In order to correct the fluctuation with time from the time of creation of calibration curve of the X-ray intensity, the correction coefficient given in the formula (6) and the formula (7) shall be calculated from the X-ray intensity of each measurement component of the bead for drift correction.

$$\alpha = \frac{(N_{s1} - N_{s2})}{(N'_{s1} - N'_{s2})} \dots\dots\dots (6)$$

$$\beta = N_{s2} - N'_{s2} \times \alpha \dots\dots\dots (7)$$

where, α : Correction coefficient (gradient coefficient)
 β : Correction coefficient (intercept coefficient)
 N_{s1} : Reference X-ray intensity of first bead for drift correction (count)
 N_{s2} : Reference X-ray intensity of second bead for drift correction (count)
 N'_{s1} : X-ray intensity of first bead for drift correction (count)
 N'_{s2} : X-ray intensity of second bead for drift correction (count)

- c) **Calculation of drift-corrected X-ray intensity** Calculate the X-ray intensity of the analysis bead and the bead for checking the analysis tolerance obtained in **8.4.5 a)** according to the formula (8), and obtain the drift-corrected X-ray intensity ⁽¹⁴⁾.

$$I = \alpha I' + \beta \dots\dots\dots (8)$$

where, I : Drift-corrected X-ray intensity of analysis bead and bead for checking the analysis tolerance
 I' : X-ray intensity of analysis bead and bead for checking the analysis tolerance (count)
 α : Correction coefficient (gradient coefficient)
 β : Correction coefficient (intercept coefficient)

Note ⁽¹⁴⁾ In **8.4.4**, when the intensity ratio method which sets the first bead for drift correction to be 1, and sets the second bead for drift correction to be 0 is used, a series of the formulae (6) to (8) is arranged, and can be expressed as the simpler formula $I = (I' - N_{s2}) / (N_{s1} - N_{s2})$.

- d) **Calculation of analytical value** Substitute the drift-corrected X-ray intensity for the calibration curve formula (9) created in **8.4.4 d)** for each measurement component, and take the calculated value obtained as the analytical value ⁽¹⁵⁾.

$$\hat{W}_i = (aI_i^2 + bI_i + c)(1 + \sum d_j \hat{W}_j) + \sum l_j \hat{W}_j \dots\dots\dots (9)$$

where, $\hat{W}_i$: Calculated value of component *I* [% (mass fraction)]

I_i : Drift-corrected X-ray intensity of component *I*

d_j : Coexisting component correction coefficient of coexisting component *J*

$\hat{W}_j$: Calculated value of coexisting component *J* [% (mass fraction)]

l_j : Overlapping correction coefficient of coexisting component *J*

a, b, c : Calibration curve coefficient

Note ⁽¹⁵⁾ In the calculation according to the coexisting component correction formula (9), calculate each analytical component one by one, and until the calculated value of each component converges to a fixed value, repeat this calculation. Usually, the number of times of repetitive operation requires about 3 times to 5 times. These are given in detail in Annex 7.

8.4.6 Evaluation of analysis tolerance Obtain the difference between the analytical value and the content (for reference material, certified value) of the bead for checking the analysis tolerance obtained in **8.4.5 d)** with respect to each measurement component, and compare with tolerances in table 2. If the difference between both is within the tolerance, take the analytical value of the analysis bead obtained in **8.4.5 d)** as the report value. When it is not within the tolerance, after performing the evaluation of the measurement condition in accordance with clause **10**, carry out the analysis in the subclause after **8.4.2** again.

Table 2 Tolerance ⁽¹⁶⁾ of analytical value

Unit : % (mass fraction)

	Material division of refractory products										
	Argilla- ceous	Quartzite	High-alumina		Magnesia	CM	ZS		AZS		AM
			Al ₂ O ₃ less than 90 %	Al ₂ O ₃ not less than 90 %			SiO ₂ less than 5 %	SiO ₂ not less than 5 %	SiO ₂ less than 5 %	SiO ₂ not less than 5 %	
SiO ₂	0.25	0.25	0.20	0.10	0.10	0.10	0.05	0.25	0.05	0.25	0.10
Al ₂ O ₃	0.20	0.10	0.25	0.25	0.05	0.25	0.10	0.10	0.25	0.25	0.25
Fe ₂ O ₃	0.05	0.05	0.05	0.05	0.05	0.25	0.05	0.05	0.05	0.05	0.05
TiO ₂	0.05	0.03	0.03	0.03	—	0.03	0.03	0.03	0.03	0.03	0.03
MnO	0.01	0.01	0.01	0.01	—	0.02	—	—	—	—	—
CaO	0.05	0.10	0.05	0.05	0.10	0.10	0.05	0.05	0.05	0.05	0.05
MgO	0.05	0.05	0.05	0.05	0.25	0.40	0.05	0.05	0.05	0.05	0.25
Na ₂ O	0.05	0.03	0.03	0.03	—	—	0.05	0.05	0.05	0.05	0.03
K ₂ O	0.05	0.02	0.05	0.05	—	—	0.05	0.05	0.05	0.05	0.02
Cr ₂ O ₃	0.05	—	—	—	—	0.30	0.05	0.05	0.05	0.05	—
ZrO ₂	0.05	—	—	—	—	—	0.30	0.30	0.05	0.05	—
P ₂ O ₅	0.05	—	—	—	—	—	0.05	0.05	—	—	0.03
HfO ₂	—	—	—	—	—	—	0.05	0.05	0.05	0.05	—

Note ⁽¹⁶⁾ However, when the content is 0.10 % to 0.50 % (mass fraction), the tolerance shall be either the value in the table or 0.03 % (mass fraction), whichever is smaller. Furthermore, when the content is not more than 0.10 % (mass fraction), the tolerance shall be either the value in the table or 0.02 % (mass fraction), whichever is smaller.

Remarks : CM: chromium-magnesia, ZS: zircon-zirconia,
AZS: alumina-zirconia-silica, AM: alumina-magnesia.

9 Record method

9.1 Arrangement of analytical values The arrangement of the analytical values shall be as follows.

- a) Express the analytical value as the percentage of a dry base, and convert it according to the following formula.

$$W'_i = \frac{W_i \times (100 - W_{LOI})}{100} \dots\dots\dots (10)$$

where, W'_i : Content of a dry base [% (mass fraction)]

W_i : Analytical value obtained in 8.4.5 d)
[% (mass fraction)]

W_{LOI} : Loss on ignition value obtained in 8.4.1 d)
[% (mass fraction)]

- b) Round off the analytical value in accordance with **JIS Z 8401** as follows.
 - 1) When the integer part of content is 2 digits, round to one decimal place.
 - 2) When the integer part of content is 1 digit or not more than 1 % (mass fraction), round to two decimal places.

9.2 Test report The following matters shall be recorded on the test report.

- a) Name of the company which conducted the analysis
- b) Date of test
- c) Analysis method (**JIS R 2216**)
- d) Sample name and information concerning samples
- e) Name of analytical component and analytical value

10 Evaluation method of measurement condition

10.1 Evaluation time The evaluation of measurement condition shall be performed in the following cases.

- a) When an analysis condition is newly set
- b) When nonconformity is judged in this evaluation
- c) When an analysis condition is changed or renewed
- d) At the time of introduction of X-ray fluorescence spectrometric analysis apparatus
- e) When a detector and an optical system, etc. of X-ray fluorescence spectrometric analysis apparatus are repaired
- f) When fusion apparatus or fusion equipment is introduced or changed
- g) When a fusion condition or a type of flux is changed
- h) When the lot of a flux is changed

10.2 Types of evaluation method of measurement condition The evaluation method of the measurement condition shall be taken as the following three types.

- a) Evaluation of glass bead mass
- b) Evaluation of setting condition of X-ray fluorescence spectrometric analysis apparatus
- c) Evaluation of uniformity between glass beads

10.3 Evaluation of glass bead mass

10.3.1 Summary Prepare six glass beads, measure the mass of the prepared glass beads, examine the vaporization or the degree of scattering, and determine the optimum fusion conditions such as fusion method, fusion temperature, fusion time.

10.3.2 Sample For the sample, select one kind of the reference material which corresponds by material of the calibration curve to create and use it ⁽¹⁷⁾.

Note ⁽¹⁷⁾ Since, for Na₂O and MgO, the sensitivity of X-ray fluorescence spectrometric analysis apparatus is low, the reference material of which the content of these components is not less than 0.5 % (mass fraction) shall be selected.

10.3.3 Preparation of bead for measurement condition evaluation The preparation operation shall be as follows.

- a) Weigh the glass bead preparation container correctly, weigh the sample, flux and oxidizing agent correctly in accordance with **8.4.2**, and prepare the glass bead in accordance with **8.4.3 a) to c)**.
- b) Weigh the glass bead obtained thus including the glass bead preparation container correctly to the nearest 0.1 mg, and obtain the mass of the glass bead.
- c) Repeat the operations in **a)** and **b)**, prepare six beads for measurement condition evaluation, and arrange the measured values of each bead as given in table 3.

Table 3 Arrangement of measured values of mass of bead for measurement condition evaluation

Glass bead number, <i>i</i>	1	2	3	4	5	6
Mass, g	m_1	m_2	m_3	m_4	m_5	m_6

10.3.4 Calculation Obtain the coefficient of variation of mass of the glass bead according to the following formula (11) using the result of the bead for measurement condition evaluation obtained in **10.3.3**.

$$CV_m = \frac{\sqrt{\frac{\sum (m_i - \bar{m})^2}{6 - 1}}}{\bar{m}} \times 100 \dots\dots\dots (11)$$

where, CV_m : Coefficient of variation of mass of bead for measurement condition evaluation (%)
 m_i : Mass of bead for *i*-measurement condition evaluation (g)
 $\bar{m}$: Average of mass of bead for measurement condition evaluation (g)

10.3.5 Evaluation Perform the evaluation of the result obtained from the formula (11) in **10.3.4** according to the formula (12), and if the formula (12) is not satisfied, perform the evaluation of the fusion condition until it is satisfied.

$$CV_m > 0.1 \dots\dots\dots (12)$$

10.4 Evaluation of setting condition of X-ray fluorescence spectrometric analysis apparatus

10.4.1 Summary Study the measurement condition of X-ray fluorescence spectrometric analysis apparatus using the bead for measurement condition evaluation obtained in **10.3.3**, and determine the optimum measurement condition.

10.4.2 Setting of X-ray fluorescence spectrometric analysis apparatus Set the X-ray fluorescence spectrometric analysis apparatus and measurement environment to the condition that the sufficient accuracy of measurement is attained.

In addition, as the X-ray fluorescence analysis conditions, for example, the conditions as given in table 4 should be set ⁽¹⁸⁾.

Note ⁽¹⁸⁾ Since the X-ray fluorescence spectrometric analysis apparatus has various kinds of types, set the optimum condition in conformity with the measurement system and performance of the apparatus.

Table 4 Example of X-ray fluorescence analysis conditions

Component	Spectral line (order)	Analyzing crystal	Detector	Counting time, s ⁽¹⁹⁾
Na ₂ O	Na K α (1)	TAP ⁽²⁰⁾	Gas-flow proportional counter	200
MgO	Mg K α (1)	TAP	Gas-flow proportional counter	100
Al ₂ O ₃	Al K α (1)	PET ⁽²¹⁾	Gas-flow proportional counter	100
SiO ₂	Si K α (1)	PET	Gas-flow proportional counter	100
P ₂ O ₅	P K α (1)	Ge	Gas-flow proportional counter	50
K ₂ O	K K α (1)	LiF200 ⁽²²⁾	Gas-flow proportional counter	20
CaO	Ca K α (1)	LiF200	Gas-flow proportional counter	20
TiO ₂	Ti K α (1)	LiF200	Gas-flow proportional counter	50
Cr ₂ O ₃	Cr K α (1)	LiF200	Scintillation counter	20
MnO	Mn K α (1)	LiF200	Scintillation counter	20
Fe ₂ O ₃	Fe K α (1)	LiF200	Scintillation counter	20
ZrO ₂	Zr L α (1)	Ge	Gas-flow proportional counter	100
HfO ₂	Hf M α (1)	PET	Gas-flow proportional counter	100

Notes ⁽¹⁹⁾ Counting time is made to be sufficiently long so that the conditions given in table 6 are satisfied.

⁽²⁰⁾ It refers to a Thallium Acid Penta-Phthalate crystal and is also called TlAP. In place of TAP, an artificial multilayer built up film can also be used.

⁽²¹⁾ It refers to a Penta-Erythritol crystal and is also called PE.

⁽²²⁾ Analyzing crystal using (200) planes of lithium fluoride

Remarks : X-ray passage: vacuum, X-ray tube: end-window rhodium target,
Applied voltage-current: 40 kV – 70 mA

10.4.3 Measurement of X-ray fluorescence intensity Select one bead from the beads for measurement condition evaluation obtained in 10.3.3 c), perform the repetitive measurement independently 6 times for each measurement component, and arrange each as given in table 5.

Table 5 Arrangement of measured values of X-ray intensity

Number of measurements, k	1	2	3	4	5	6	Average
Measured values, integrated counts ⁽²³⁾	X_1	X_2	X_3	X_4	X_5	X_6	$\bar{X}$

Note ⁽²³⁾ For the apparatus indicating the X-ray intensity per a fixed time, the value obtained by multiplying the average X-ray intensity by the measurement time is used.

10.4.4 Evaluation of whether X-ray intensity satisfies the basic value Perform the evaluation of the average of the measured values obtained in table 5 according to the formula (13), and if the formula (13) is not satisfied, repeat the change of the measurement condition in table 4 and the measurement in **10.4.3** until it is satisfied. If the measured value of X-ray intensity of the specific measurement component does not satisfy the basic value by any means, the determination by this method cannot be applied to the measurement component.

$$\bar{X} \geq C_m \dots\dots\dots (13)$$

where, $\bar{X}$: Average of measured values of X-ray intensity (count)
 C_m : Basic value for the content of each component obtained from table 6 (count)

Table 6 Evaluation basic value of measured values of X-ray fluorescence intensity

Content, % (mass fraction)	Basic value (C_m), count ⁽²³⁾
70 or over	2 000 000
50 to 69.9	1 500 000
30 to 49.9	1 000 000
10 to 29.9	500 000
5 to 9.99	150 000
3 to 4.99	50 000
1 to 2.99	20 000
0.50 to 0.99	10 000
0.49 or under	5 000

10.4.5 Evaluation of repetitive measurement accuracy of X-ray fluorescence spectrometric analysis apparatus Obtain the simple repetitive measurement accuracy of the X-ray fluorescence spectrometric analysis apparatus according to the formula (14) and perform the evaluation according to the formula (15). If the X-ray intensity of the measurement component does not satisfy the formula (15), since the body of X-ray fluorescence spectrometric analysis apparatus or the measurement environment has some sort of problem, adjust it, and then perform the operation after **10.4.1**. If the average value ($\bar{X}$) of X-ray intensity of the measurement component does not satisfy the basic value by any means, do not perform the determination of the component ⁽²⁴⁾.

$$CV_x = \frac{\sqrt{\frac{\sum (X_k - \bar{X})^2}{6-1}}}{\bar{X}} \times 100 \dots\dots\dots (14)$$

$$CV_x < 2.0 \times \frac{100}{\sqrt{\bar{X}}} \dots\dots\dots (15)$$

where, CV_x : Coefficient of variation of repetitive measurement of measurement component (%)

X_k : K th measured value of X-ray intensity (count) ⁽²³⁾

$\bar{X}$: Average of measured values of X-ray intensity (count) ⁽²³⁾

Note ⁽²⁴⁾ The component which cannot be analyzed with the X-ray fluorescence spectrometric analysis method can be analyzed with a chemical analysis method as specified in **JIS R 2212-1 to -5**, **JIS R 2012**, **JIS R 2013**, and **JIS R 2014**.

10.4.6 Evaluation of uniformity of glass bead If the conditions in **10.4.5** are satisfied, perform the evaluation of uniformity of the glass bead according to the following procedure.

- a) **Measurement of main component of six glass beads** Perform the measurement of the X-ray intensity of the measurement component of not less than 8 % (mass fraction) in content in the sample of six glass beads obtained in **10.3.3**, and arrange each measurement component as given in table 7.

Table 7 Arrangement of measured values of uniformity

Number of measurement, i	1	2	3	4	5	6	Average
Measured values, integrated counts ⁽²³⁾	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	$\bar{Y}$

- b) **Calculation of uniformity** Obtain the uniformity of glass bead using the measurement component of not less than 8 % (mass fraction) in content in the sample according to the formula (16).

$$\sigma = \frac{\sqrt{\frac{\sum (Y_i - \bar{Y})^2}{6-1}}}{\bar{Y}} \times Z \dots\dots\dots (16)$$

where, σ : Standard deviation of measurement component [% (mass fraction)]
 Z : Content of measurement component [% (mass fraction)]
 Y_i : Measured values of X-ray intensity of i -bead for measurement condition evaluation (count)
 $\bar{Y}$: Average of measured values of X-ray intensity of bead for measurement condition evaluation (count)

- c) **Evaluation of uniformity of glass bead** Based on the result obtained according to the formula (16), perform the evaluation of uniformity of glass bead according to the formula (17). If this condition is not satisfied, perform the study of the glass bead preparation method in **10.3.3** until it is satisfied.

$$\left. \begin{array}{l} \text{When } Z > 40, \sigma < 0.15 \\ \text{When } 8 \leq Z \leq 40, \sigma < 0.10 \end{array} \right\} \dots\dots\dots (17)$$

Annex 1 (normative)

Conditions to be satisfied by refractory series reference materials

1 Scope This Annex specifies the conditions to be satisfied by refractory series reference materials.

2 Material of refractory series reference materials The refractory series reference materials shall be taken as the following eight materials.

- a) Argillaceous series reference materials
- b) Quartzite series reference materials
- c) High-alumina series reference materials
- d) Magnesite series reference materials
- e) Chromium-magnesite series reference materials
- f) Zircon-zirconia series reference materials
- g) Alumina-zirconia-silica series reference materials
- h) Alumina-magnesite series reference materials

3 Conditions to be satisfied The refractory series reference materials shall be prepared in accordance with **ISO/IEC Directives: 1992 part 2** and **JIS Q 0034**, and shall satisfy all conditions of a) to f) below.

- a) The refractory series reference materials shall consist of the reference material of 10 kinds or more per series for each material in order to perform the X-ray fluorescence analysis of refractory brick and refractory mortar.
- b) The range of the chemical composition which constitutes each series shall be prepared so that the determination limit in table 1 of the text can be broadly interpolated.
- c) The value of each component shall exist stepwise within a series, and the allocation of the content into a series shall be independent of other components.
- d) The powdered sample prepared in grain size of not more than 106 μm without segregation shall satisfy the requirements specified in clause 4 below.
- e) The refractory series reference materials shall be stably supplied. Therefore, two series or more for each material shall be prepared as required.
- f) For the certified value, the value determined correctly by the chemical analysis method specified in Japanese Industrial Standard and the chemical analysis method in conformity with this method shall be statistically processed in accordance with **JIS Q 0035** and certified.

4 Preparation, storage and marking

4.1 Preparation method The preparation shall be performed according to the following method.

- a) Perform the whole design of the reference material which constitutes a series by each material, and determine the number of the individual reference materials which constitutes one series and the chemical composition and preparation (for example, 50 kg/one material) of each individual reference material.
- b) In order to realize the composition determined in **a)**, combine refractory bricks and refractory materials ⁽¹⁾, and after molding, fire until they sinter.
- c) Grind the sintered with a jaw crusher, a roll crusher, a top grinder, etc., and remove contaminations such as iron.
- d) Put this ground object into the most homogeneous possible grinder or the grinder of the material (alumina, mullite, etc.) which consists of components which constitute analytical items, and perform the fine grinding at once. When the fine grinding is not performed at once, finally, put all the fine-ground objects into a large-sized mixer, and mix at least for 10 h.
- e) Take the sample from each section of the fine-ground objects, and confirm that there is no segregation by performing the analysis.

Note ⁽¹⁾ Other burned bricks are combined on the basis of burned bricks. When the target composition is not acquired only by these, reagents or industrial chemicals are added. Avoid halides, sulfates, phosphates, borates and carbonates of alkali metal because they remain easily also after burning.

4.2 Storage The storage shall be performed as follows.

- a) For the prepared reference material, clearly indicate the name of each reference material on the location which is not affected by temperature, humidity, direct sunlight, and vibration, and store it under the dry condition.
- b) Appoint a manager, and confirm the storage situation periodically.

4.3 Marking The reference material shall be put into the glass container with a stopper, and the following shall be marked. However, **b)** to **h)** may be written in a description.

- a) Designation and kind
- b) Component and certified value
- c) Analysis station which participated in a joint drift correction experiment
- d) Analysis method used for decision of certified value
- e) Name of analysis institution
- f) Preparation date
- g) Handling precautions
- h) Name of preparation and distribution institution

5 Certified value

5.1 Analysis method The analysis method shall be as specified in **JIS R 2012, JIS R 2013, JIS R 2014** and **JIS R 2212-1 to -5**.

5.2 Analysis station The analysis station shall be provided with the following requirements.

- a) The analysis station shall be provided with the expert in chemical analysis of a refractory brick and refractory mortar, and the control of analysis accuracy shall be sufficiently performed.
- b) The analysis station shall be equipped with all the facilities specified in **JIS R 2012, JIS R 2013, JIS R 2014**, and **JIS R 2212-1 to -5**.
- c) The number of the analysis stations shall be not less than eight.

5.3 Certified value The certified value shall be expressed by the average of the analytical values of two times of analysis which each analysis station performed by changing a day. The certified value shall be expressed by the increased number of digits by one compared with the number of digits shown in the report value of **9.1 b)** of the text.