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**Methods for chemical analysis of
fine silicon nitride powders for fine
ceramics**

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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 Advanced Industrial Science and Technology (AIST) 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 1603** : 1994 is replaced with this Standard.

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Methods for chemical analysis of fine silicon nitride powders for fine ceramics

1 Scope

This Japanese Industrial Standard specifies the methods for chemical analysis of fine silicon nitride powders used as the raw material for manufacture of fine ceramics.

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 0115 *General rules for molecular absorptiometric analysis*

JIS K 0116 *General rules for atomic emission spectrometry*

JIS K 0127 *General rules for ion chromatographic analysis*

JIS K 0557 *Water used for industrial water and wastewater analysis*

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

JIS K 8005 *Reference materials for volumetric analysis*

JIS K 8007 *General rule for test methods of highly purified reagents*

JIS R 6003 *Method for sampling of abrasive grains*

JIS Z 8401 *Guide to the rounding of numbers*

3 General items

General items common to the analysis method shall be in accordance with **JIS K 0050, JIS K 0115, JIS K 0116, JIS K 0127, JIS K 8001 and JIS K 8007.**

4 Analysis items

Analysis items specified in this Standard shall be as follows.

- a) Total silicon (T.Si)
- b) Total nitrogen (T.N)
- c) Aluminium (Al)
- d) Iron (Fe)
- e) Calcium (Ca)
- f) Oxygen (O)
- g) Carbon (C)

- h) Fluorine (F)
- i) Chlorine (Cl)

5 Sampling and handling of sample

5.1 Sampling

Take analytical samples in accordance with **JIS R 6003**.

5.2 Handling of sample

Put about 5 g of analytical sample into a flat-type weighing bottle (50 mm × 30 mm). Dry it in an air bath at 110 °C for 2 h. Cool it as it is in a desiccator (desiccant : magnesium perchlorate for drying) and preserve it.

5.3 Weighing method of sample

Weigh out the analytical sample of the required quantity to the nearest 0.1 mg using a chemical balance.

6 Obtaining analytical values

6.1 Number of analyses

Analyze the same component twice on different days.

6.2 Blank test

Upon analysis, perform a blank test to correct the measured values.

6.3 Indication of analytical values

The analytical values shall be indicated in % (mass fraction) in dry state, and rounded off as follows in accordance with **JIS Z 8401**.

- a) For the total silicon and total nitrogen, round off the figure to the first decimal place.
- b) For other components, round off the figure to the second decimal place.

6.4 Investigation and adoption of analytical values

- a) When the difference between two analytical values does not exceed the tolerance shown in table 1, the average value shall be reported.
- b) When the difference between two analytical values exceeds the tolerance shown in table 1, perform additional two analyses. When the difference does not exceed the tolerance, the average value thereof shall be reported. If the difference also exceeds the tolerance, the median of four analytical values shall be reported.

Table 1 Tolerances on analytical values

Unit : % (mass fraction)

Component	T.Si	T.N	Al ^{c)}	Fe ^{c)}	Ca ^{c)}	O	C	F	Cl
Tolerance	0.15	0.15 ^{a)} 0.35 ^{b)}	0.001 0.005	0.001 0.003	0.001 0.012	0.090	0.020	0.010	0.005
Notes ^{a)} Pressurized acid decomposition – Water vapour distillation separation – Neutralization titration method ^{b)} Inert gas fusion – Thermal conductivity method ^{c)} The upper row values shall apply to the content rate of under 0.01 % (mass fraction) and the lower row values shall apply to the content rate of 0.01 % (mass fraction) or over.									

7 Determination method of total silicon

7.1 Classification of determination method

The total silicon shall be determined in either of the following methods.

- Dehydrated mass determination and ICP (inductively coupled plasma, hereafter referred to as "ICP") emission spectrometry combined method : This method shall apply to the sample of which the total content rate of silicon is 30 % (mass fraction) or over to and including 70 % (mass fraction).
- Agglomerated mass determination and ICP emission spectrometry combined method : This method shall apply to the sample of which the total content rate of silicon is 30 % (mass fraction) or over to and including 70 % (mass fraction).

7.2 Dehydrated mass determination and ICP emission spectrometry combined method

7.2.1 Summary

Fuse the sample with sodium carbonate and dissolve it with hydrochloric acid, dehydrate silicate by evaporating to dryness, dissolve soluble salts with hydrochloric acid and filtrate. Ignite and weigh the precipitate, add hydrofluoric acid to vaporize silicon dioxide, then ignite again and weigh it. Obtain the amount of primary amount of silicon dioxide from the weight loss. Obtain the dissolved silicon amount with ICP emission spectrometry by taking filtrate. Calculate the total silicon content rate from both.

7.2.2 Reagents

Reagents used in this Standard shall be the highest purity of products on the market, and as follows. Reagent solutions shall be preserved in plastic bottles. The standard solutions shall be the products on the market conforming to Japan Calibration Service System (JCSS) or the equivalent products, and those traceable to SI units shall be used.

- Water** A3 or superior specified in table 1 of **JIS K 0557** : 1998.
- Hydrochloric acid**
- Hydrochloric acid (1+1, 1+4, 1+50)**
- Hydrofluoric acid**

- e) **Sulfuric acid (1+1, 1+4)**
- f) **Sodium carbonate (anhydrous)** ¹⁾
- g) **Standard silicon solution (1.0 mg Si/ml)**
- h) **Standard silicon solution (0.1 mg Si/ml)** Prepare by taking exactly 10 ml from the solution of **g)** in a 100 ml volumetric flask every time when necessary, diluting it with water up to the marked line and shaking to mix it.

Note ¹⁾ Potassium sodium carbonate may be used.

7.2.3 Containers

For containers to be used for various operations, glass products or plastic products ²⁾ shall be used. Meters made of plastics shall be verified beforehand. Glass products shall not be used for other operation than that specified. For the washing and preservation of containers, remove contaminants, wash with water sufficiently and preserve by filling with water in accordance with (1), (2) and (3) of clause 6 of **JIS K 8007 : 1992**.

Note ²⁾ Products made of polyethylene, polypropylene, tetrafluoroethylene resin and the like are available.

7.2.4 Weighing amount of sample

The weighing amount of sample shall be 0.30 g.

7.2.5 Operation

The determination operation shall be according to the following procedure.

- a) Weigh out the sample in a platinum dish (for example, No. 75), add 2.0 g of sodium carbonate (anhydrous), mix it and spread it uniformly over the bottom of dish. Initially heat it at a low temperature and finally ignite at about 1 000 °C to fuse it completely.
- b) Cool it as it is by covering with a watch glass and add 20 ml of hydrochloric acid (1+1). Heat and dissolve it on a water bath, wash the watch glass with small amount of water and remove, then evaporate it to dryness. During this, use a glass rod with a flattened tip to crush the deposited salts into powders at times. Cool it as it is, add 5 ml of hydrochloric acid and leave it for about 1 min, add 20 ml of hot water and heat it on a water bath for about 5 min to dissolve soluble salts.
- c) Filtrate the insoluble residue with filter paper (Class 5 B), and wash it with hot hydrochloric acid (1+50) several times and with hot water sufficiently. Receive the filtrate and washings in a 250 ml volumetric flask, cool it as it is, dilute it with water up to the marked line and shake to mix it.
- d) Put the precipitate of **c)** into a platinum crucible (for example, No. 30) with filter paper, add 5 drops of sulfuric acid (1+4), heat it by keeping not to catch fire and reduce the filter paper to ashes, then ignite it at 1 100 °C ± 25 °C for 60 min. After cooling it as it is in a desiccator, weigh out the mass. Repeat this operation until reaching the constant mass.
- e) Moisten silicon dioxide of **d)** with water, add 3 drops of sulfuric acid (1+1) and 10 ml of hydrofluoric acid, and evaporate it to dryness on a sand bath. Ignite it at 1 100 °C ± 25 °C for 5 min, cool it as it is in a desiccator and weigh out the mass. The loss of mass shall be the primary silicon dioxide.

- f) Take exactly 10 ml from the solution of **c**) in a 100 ml volumetric flask, add 5 ml of hydrochloric acid (1+4), dilute it with water up to the marked line, and shake to mix it.
- g) Spray a portion of the solution of **f**) into the argon plasma of ICP emission spectrometer and measure the emission intensity, for example, at 251.61 nm in wavelength ³⁾.

Note ³⁾ For the determination of the dissolved silicon, molybdenum blue absorptiometry may be used. In this case, take exactly 10 ml from the solution of **c**) in a plastic beaker (100 ml), add 2 ml of hydrofluoric acid (1+9), leave it for 10 min as it is, add 50 ml of boric acid solution and 2 ml of hydrochloric acid (1+4), and dilute it with water up to about 70 ml. Add 3 ml of hexaammonium heptamolybdate solution, stir it and leave it for 10 min as it is. Add 5 ml of tartaric acid solution and 3 ml of L-ascorbic acid solution sequentially and stir them each time. Transfer it into a 100 ml volumetric flask, dilute with water up to the marked line, shake to mix it and leave it for 30 min as it is. Take a portion of this solution in a cell (1 cm) of absorptiometer and measure the absorbance at the neighbourhood of 650 nm in wavelength by taking the water as the reference solution.

In this case, the reagents shall be as follows.

- 1) **Hydrofluoric acid (1+9)**
- 2) **Boric acid solution (40 g/L)**
- 3) **Hexaammonium heptamolybdate solution** Dissolve 50 g of hexaammonium heptamolybdate tetrahydrate in warm water, filtrate it if necessary, and make it 500 ml with water. When any molybdate is precipitated during preservation, prepare it newly.
- 4) **Tartaric acid solution (100 g/L)**
- 5) **L-ascorbic acid solution (100 g/L)** Preserve it at a cool and dark place. When two weeks elapsed after preparation, it should not be used.

7.2.6 Blank test

Perform operations of **7.2.5** without using the sample, provide that the fusing operation is omitted. Take the solution corresponding to **7.2.5 c**) as the blank test solution.

7.2.7 Preparation of working curve

Take exactly 10 ml from the blank test solution of **7.2.6** in several 100 ml volumetric flasks and add 0 ml to 4 ml stepwise and exactly from the standard silicon solution respectively. For each, add 5 ml of hydrochloric acid (1+4) gradually, dilute it with water up to the marked line and shake to mix it. Perform operations of **7.2.5 g**) by using these solutions for working curve, prepare the relation curve between the emission intensity obtained and the amount of silicon, translate it so as to pass the origin, and take it as the working curve ⁴⁾.

Note ⁴⁾ When using the molybdenum blue absorptiometry, it shall be as follows. Take exactly 0 ml to 3 ml stepwise from the standard silicon solution in several plastics beakers (100 ml) and add exactly 10 ml from the blank test solution respectively. For each, perform subsequent operations of addition of hydrofluoric acid (1+9) of Note ³⁾ of **7.2.5 g**), prepare the relation curve between the absorbance obtained and the amount of silicon, translate it so as to pass the origin, and take it as the working curve.

7.2.8 Calculation

Obtain the amount of dissolved silicon from the emission intensity obtained in **7.2.5 g)** and **7.2.6** and the working curve prepared in **7.2.7**, and calculate the total silicon content rate in sample according to the following equation.

$$T.Si = \frac{[(m_1 - m_2) \times 0.4674 + (A_1 - A_2) \times 250 / 10]}{m} \times 100$$

where, $T.Si$: Total silicon content rate [% (mass fraction)]

m_1 : Amount of primary silicon dioxide of **7.2.5 e)** (g)

m_2 : Amount of silicon dioxide of **7.2.6** (g)

A_1 : Amount of dissolved silicon of **7.2.5 g)** (g)

A_2 : Amount of dissolved silicon of **7.2.6** (g)

m : Weighing amount of sample (g)

7.3 Agglomerated mass determination and ICP emission spectrometry combined method

7.3.1 Summary

Fuse the sample with sodium carbonate and boric acid, dissolve it with hydrochloric acid, agglomerate silicate by adding polyethylene oxide and filtrate. Ignite and weigh the precipitate, add hydrofluoric acid to vaporize silicon dioxide, then ignite again and weigh it. Obtain the amount of primary amount of silicon dioxide from the weight loss. Obtain the dissolved silicon amount with ICP emission spectrometry by taking filtrate. Calculate the total silicon content rate from both.

7.3.2 Reagents

Reagents shall be in accordance with **7.2.2** and as given below. The reagent of **b)** shall be preserved in a plastic bottle.

a) **Boric acid**

b) **Polyethylene oxide solution** Dissolve 0.1 g of polyethylene oxide gradually in 200 ml of water by stirring. When two weeks elapsed after preparation, it shall not be used.

c) **Cellulose powder**

7.3.3 Containers

In accordance with **7.2.3**.

7.3.4 Weighing amount of sample

The weighing amount of sample shall be 0.30 g.

7.3.5 Operation

The determination operation shall be according to the following procedure.

a) Weigh out the sample in a platinum dish (for example, No. 75), add 1.5 g of sodium carbonate (anhydrous) and 0.2 g of boric acid and mix, and spread it uniformly over the bottom of dish. Initially heat it at a low temperature and finally ignite at 1 000 °C or over to fuse it ⁵⁾.

- b) Cool it as it is by covering with a watch glass, then add 20 ml of hydrochloric acid (1+1). Heat and dissolve it on a water bath until it becomes jelly-like, remove the watch glass without washing, add 0.05 g of cellulose powder and 10 ml of polyethylene oxide solution, then stir and leave them for about 5 min.
- c) Filtrate the insoluble residue with filter paper (Class 5 B), wash the platinum dish and watch glass with hot hydrochloric acid (1+50) several times and with hot water sufficiently. Receive the filtrate and washings in a 250 ml volumetric flask, cool it as it is, dilute it with water up to the marked line and shake to mix it.
- d) Perform operations of **d)** and **e)** of **7.2.5** on the precipitate and filter paper of **c)** in the same way.
- e) Take exactly 10 ml from the solution of **c)** and perform operations of **f)** and **g)** of **7.2.5** in the same way ⁶⁾.

Notes ⁵⁾ When fusing time is too long, the fused substance becomes less soluble in hydrochloric acid.

- ⁶⁾ For the determination of dissolved silicon, molybdenum blue absorptiometry may be used. In this a case, perform operations of Note ³⁾ of **7.2.5 g)** in the same way provided that the addition amount of hydrochloric acid (1+4) of **7.2.5 f)** shall be 1 ml.

7.3.6 Blank test

Perform operations of **7.3.5** without using the sample, provided that the fusing operation is omitted. Take the solution corresponding to **7.3.5 c)** as the blank test solution.

7.3.7 Preparation of working curve

Take exactly 10 ml from the blank test solution of **7.3.6** in several 100 ml volumetric flasks respectively, then perform subsequent operations of the addition of standard silicon solution of **7.2.7**.

7.3.8 Calculation

In accordance with **7.2.8**.

8 Determination method of total nitrogen

8.1 Classification of determination method

The total nitrogen shall be determined in either of the following methods.

- a) Pressurized acid decomposition – water vapour distillation separation – neutralization titration method : This method shall apply to the sample of which the total content rate of nitrogen is 20 % (mass fraction) or over to and including 45 % (mass fraction).
- b) Inert gas fusion – thermal conductivity method : This method shall apply to the sample of which the total content rate of nitrogen is 0.01 % (mass fraction) or over to and including 50 % (mass fraction).

8.2 Pressurized acid decomposition – water vapour distillation separation – neutralization titration method

8.2.1 Summary

Decompose the sample in a pressure decomposition vessel with sulfuric acid and hydrofluoric acid and convert nitrogen into ammonium salt. Add boric acid and transfer them to a distilling flask. Add sodium hydroxide and perform water vapour distillation. Let the distilled ammonium absorb to a certain amount of amidosulfuric acid and titrate the excessive amidosulfuric acid with sodium hydroxide.

8.2.2 Reagents

Reagents shall be in accordance with 7.2.2 and as given below. The reagents of **b)**, **e)** and **h)** shall be preserved in a plastic bottle.

- a) **Water** In accordance with 7.2.2 a).
- b) **Hydrofluoric acid**
- c) **Sulfuric acid (1+1)**
- d) **Boric acid**
- e) **Sodium hydroxide solution (500 g/L)**
- f) **Ammonium sulfate** 99.9 % (mass fraction) or over. Dry at 110 °C for 3 h and cool as it is in a desiccator.
- g) **0.1 mol/L amidosulfuric acid solution** Weigh out 10.0 g of amidosulfuric acid of **b)** in clause 4 of **JIS K 8005 : 2006** to the nearest 0.1 mg, dissolve it in water and dilute it exactly to 1 000 ml. Calculate the factor of this solution according to the following equation.

$$F = \frac{G \times P}{9.7093 \times 100}$$

where, F : Factor of 0.1 mol/L amidosulfuric acid solution

G : Weighing amount of amidosulfuric acid (g)

P : Purity of amidosulfuric acid [% (mass fraction)]

- h) **0.1 mol/L sodium hydroxide solution** The preparation method and the storage method shall be in accordance with (19.4) in 4.5 of **JIS K 8001 : 1998**. Obtain the factor of this solution as follows. Take exactly 50 ml of 0.1 mol/L amidosulfuric acid solution in a beaker (200 ml), dilute it with water up to about 100 ml. Use a glass electrode pH meter and titrate it with 0.1 mol/L sodium hydroxide solution. Take the end point as pH 5.5 and obtain the volume of 0.1 mol/L sodium hydroxide solution used. Calculate the factor of this solution according to the following equation.

$$F'' = \frac{F \times 50.00}{V}$$

where, F'' : Factor of 0.1 mol/L sodium hydroxide solution

F : Factor of 0.1 mol/L amidosulfuric acid solution

V : Volume of 0.1 mol/L sodium hydroxide solution used (ml)

8.2.3 Apparatus and instrument

Apparatus and instrument shall be as follows.

- a) **Pressure decomposition vessel** In general, a pressure decomposition vessel on the market shall be used. An example is shown in figure 1.

The inner lid and plastic vessel ⁷⁾ shall be made of tetrafluoroethylene resin, and the outer lid, balance plate and pressure vessel shall be made of stainless steel.

Note ⁷⁾ When using the plastic vessel which has contained nitric acid, nitrogen will give a low value. For total nitrogen determination analysis, an exclusive vessel shall be used.

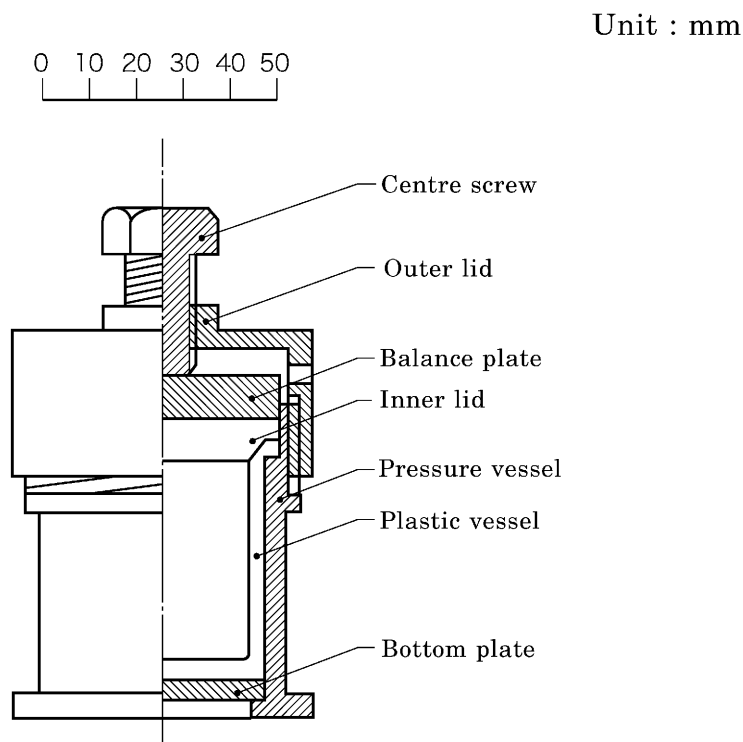


Figure 1 Pressure decomposition vessel

- b) **Water vapour distillation apparatus** In general, the following instruments shall be coupled as shown in figure 2.

Each instrument shall be made of hard glass, coupled by common ground joints and be fixed by springs or clamps.