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JAPANESE INDUSTRIAL STANDARD

Methods for Chemical Analysis of Limestone

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Methods for Chemical Analysis of Limestone

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1. Scope

This Japanese Industrial Standard specifies the methods for chemical analysis of limestone.

2. General Matters

The general matters common to the methods for chemical analysis shall be in accordance with JIS K 0050, JIS K 0115 and JIS K 0121.

3. Items for Chemical Analysis

The items ⁽¹⁾ for chemical analysis specified in this standard shall be as follows:

Ignition loss (Ig. loss)

Silicon dioxide (SiO_2)

Iron (III) oxide (Fe_2O_3)

Aluminium oxide (Al_2O_3)

Calcium oxide (CaO)

Magnesium oxide (MgO)

Phosphorus pentaoxide (P_2O_5)

Total sulfur (Total S)

Note ⁽¹⁾ Silicon dioxide (excepting gravimetric analysis), iron (III) oxide, aluminium oxide, calcium oxide, magnesium oxide and phosphorus pentaoxide are conveniently marked with oxide state, though determined as elemental state respectively.

4. Methods of Sampling and Handling

4.1 For the sample of analysis, take care of expressing the mean value by sufficient mixing, and further confirm that there is no mixing of foreign substances.

4.2 For the sample of analysis, thinly spread about 10 g of that crushed so that the whole amount passes the sieve of 149 μm specified in JIS Z 8801 in a flat weighing bottle (50 mm in diameter). After drying it in an air bath at 105 to 110°C for not less than 1 h, weigh out the sample from that stored in a desiccator.

4.3 For weighing out the sample of analysis, use a chemical balance and measure the specified amount to place of 0.1 mg.

Applicable Standards: See page 29.

5. Rounding off of Analytical Value

5.1 The analytical results shall be expressed with percentage and rounded off according to JIS Z 8401 as follows:

- (1) For ignition loss and calcium oxide, the analytical results shall be rounded off to one place of decimal.
- (2) For silicon dioxide, iron (III) oxide, aluminium oxide, magnesium oxide and total sulfur, the analytical results shall be rounded off to two places of decimals.
- (3) For phosphorus pentaoxide, the analytical results shall be rounded off to three places of decimals.

5.2 For analysis, a blank test shall be carried out through all operations, and the measured values shall be corrected.

5.3 The analysis shall generally be repeated not less than two times concerning the same sample. When the difference between those results exceeds the numerical value given in the tolerance (%) of Table 1, the mean value of those within the tolerance shall be calculated by analyzing again.

Table 1. Tolerance ⁽²⁾

Unit: %

Ignition loss	Silicon dioxide				Iron (III) oxide	
	Gravimetric method		Absorptiometry		Absorptiometry	
	Division	Tolerance	Division	Tolerance	Division	Tolerance
0.3	0.10 and over to 1.00 excl.	0.04	Less than 0.20	0.02	Less than 0.10	0.02
	Not less than 1.00	0.07	0.20 and over to 1.20 excl.	0.05	0.10 and over to 0.50 excl.	0.03
					0.50 and over to 1.50 excl.	0.05

Iron (III) oxide		Aluminium oxide				Calcium oxide
Atomic absorption method		Titration method		Atomic absorption method		
Division	Tolerance	Division	Tolerance	Division	Tolerance	
Less than 0.10	0.02	Less than 0.10	0.02	Less than 0.10	0.02	0.3
0.10 and over to 0.50 excl.	0.04	0.10 and over to 0.50 excl.	0.04	0.10 and over to 0.50 excl.	0.04	
0.50 and over to 1.00 excl.	0.06	Not less than 0.50	0.06	0.50 and over to 1.00	0.06	

Magnesium oxide				Phosphorus pentaoxide	
Titration method		Atomic absorption method		Absorptiometry of molybdate blue	
Division	Tolerance	Division	Tolerance	Division	Tolerance
0.50 and over to 1.00 excl.	0.10	Less than 1.00	0.05	Less than 0.010	0.002
Not less than 1.00	0.12	1.00 and over to 5.00 excl.	0.10	0.010 and over to 0.050 excl.	0.004
				0.050 and over to 1.000 excl.	0.008

Phosphorus pentaoxide		Total sulfur
Absorptiometry of phosphorus vanado molybdate		
Division	Tolerance	
0.030 and over to 0.100 excl.	0.008	0.02
Not less than 0.100	0.015	

Note (2) When two analytical values cover two classes, the tolerance of the division corresponding to the mean value of the two analytical values, shall be applied to.

6. Method for Determination of Ignition Loss

6.1 Classification of Methods The method for determination of ignition loss shall be in accordance with the gravimetric method.

6.2 Gravimetric Method

6.2.1 Summary When the sample is ignited to constant weight at $1050 \pm 50^\circ\text{C}$, the decreased amount is measured.

6.2.2 Weighed Out Amount of Sample For the sample, 1.0 g of it shall be weighed out.

6.2.3 Operation The operation of determination shall be carried out according to the following procedures:

- (1) Weigh out the sample into a platinum crucible (for example No. 30) (3), and cover it by opening a little gap. At first heat it at a low temperature, and gradually raise the temperature. At last ignite it in an electric arc furnace at $1050 \pm 50^\circ\text{C}$ for 1 h. After leaving it cooled in a desiccator by closely sealing the cover, measure the mass.
- (2) Repeat ignition every 15 min and obtain the decreased amount when it has become constant weight (4).

6.2.4 Calculation The ignition loss in the sample shall be calculated from the following formula:

$$\text{Ignition loss (\%)} = \frac{w_1 - w_2}{W} \times 100$$

where w_1 : mass of platinum crucible containing sample before ignition (g)

w_2 : mass of platinum crucible containing sample after ignition (g)

W : weighed out amount of sample (g)

Notes (³) A porcelain crucible may be used.

(⁴) Constant weight can generally be obtained by ignition for 1 h.

7. Method for Determination of Silicon Dioxide

7.1 Classification of Methods The method for determination of silicon dioxide shall be according to either of the following methods:

- (1) Perchloric Acid Dehydration Gravimetry This method shall apply to the sample having the silicon dioxide content of not less than 0.10 %.
- (2) Absorptiometry of Molybdate Blue This method shall apply to the sample having the silicon dioxide content of less than 1.20 %.

7.2 Perchloric Acid Dehydration Gravimetry

7.2.1 Summary Resolve the sample with hydrochloric acid and perchloric acid, and generate white fume by heating. Make silicic acid insoluble and filter it. Ignite the precipitates and measure the mass. Add hydrofluoric acid and volatilize silicon dioxide by heating. Thereafter, ignite it again and measure the mass. Obtain the difference of mass between the before and the after one.

7.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1+1, 1+100)
- (2) Perchloric acid (60 %)
- (3) Hydrofluoric acid

7.2.3 Weighed Out Amount of Sample For the sample, 1.0 g of it shall be weighed out.

7.2.4 Operation The operation of determination shall be carried out according to the following procedures:

- (1) Weigh out the sample into a beaker (200 ml) (⁵) and make it slurry by adding a little amount of water. Cover it with a watch glass and gradually add 5 ml of hydrochloric acid (1+1) from the brim of beaker. After the end of violent reaction, wash the watch glass with a small amount of water and remove it.
- (2) Add 5 ml of perchloric acid and heat it on a sand bath. When thick white fume of perchloric acid begins to be generated, cover it with a watch glass again. Successively heat it for 10 min.

- (3) After cooling it for a little while, add 5 ml of hydrochloric acid (1+1) and about 50 ml of warm water and mix it by shaking. When insoluble matter is almost precipitated, immediately filter it with a filter paper (Class 5 B) and several times wash it with hot hydrochloric acid (1+100). Further, sufficiently wash it with hot water ⁽⁶⁾. Receive the filtrate and washings into a beaker (300 ml) and store it.
- (4) Put insoluble matter together with the filter paper into a platinum crucible (for example, No. 30), and dry it. After incinerating the filter paper by gradually heating so that no flame is generated, ignite it at $1050 \pm 50^\circ\text{C}$ for 1 h. After leaving it cooled in a desiccator, measure the mass and repeat ignition to constant weight ⁽⁴⁾.
- (5) Get insoluble matter wet with 2 or 3 drops ⁽⁷⁾ of perchloric acid, and add 5 ml of hydrofluoric acid. Evaporate it to dryness by heating on a sand bath. Ignite it at $1050 \pm 50^\circ\text{C}$ for 10 min. After leaving it cooled in the desiccator, measure its mass.

Further, store the platinum crucible attached with residual matter as it is.

7.2.5 Calculation The silicon dioxide content in sample shall be calculated from the following formula:

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

where w_1 : mass measured in 7.2.4 (4) (g)

w_2 : mass measured in 7.2.4 (5) (g)

W : weighed out amount of sample (g)

Notes ⁽⁵⁾ For the sample containing a great amount of foreign matter, preliminarily heat the weighed out sample in a porcelain crucible at 500 to 600°C . After resolving organic substance, transfer it into a beaker.

⁽⁶⁾ When washing is insufficient, there is some fear of dispersion with explosion at incineration. Special caution should be taken for the case where a great amount of insoluble matter exists.

⁽⁷⁾ When there is a great amount of insoluble matter, the sample amount should properly be increased.

Remark: Especially when the determination of silicon dioxide is not required due to very little amount of it, the insoluble matter may be marked with acid insoluble residue by omitting the operation of 7.2.4 (5). In this case, a porcelain crucible may be used for ignition of insoluble matter.

7.3 Absorptiometry of Molybdate Blue

7.3.1 Summary Fuse the sample with sodium carbonate, and make it a certain amount by dissolving it with water. Filter this solution and partially take a part of the filtrate. After regulating the concentration of acid by adding hydrochloric acid, add ammonium molybdate and generate silicon molybdate. After removing the effect of phosphorus by adding tartaric acid, colorate molybdate blue by adding ascorbic acid and measure the absorbance.

7.3.2 Reagents The reagents shall be as follows. However, the reagent of (3) to (6) shall be stored in a plastic bottle.

- (1) Hydrochloric acid (1+1, 1+4)
- (2) Sodium carbonate (anhydride)
- (3) Ammonium molybdate solution For the ammonium molybdate solution, dissolve 25 g of ammonium molybdate (4 hydrate) with warm water and make it 500 ml. It should be filtered if necessary. However, when molybdic acid is deposited while stored, prepare it freshly.
- (4) Tartaric acid solution (10 W/v %)
- (5) Ascorbic acid solution (5 W/v %) The ascorbic acid shall be stored in a cold dark place. However, when it is colored during stock, it shall freshly be prepared.
- (6) Standard silicon dioxide solution (0.1mgSiO₂/ml) Take silicon dioxide (anhydrous silicic acid, sedimentated) (JIS K 8885) into a porcelain crucible. After igniting it at 1050±50°C for about 1 h, weigh out 0.100 g of that leaved as cooled in a desiccator into a platinum crucible. After mixing it with 1 g of sodium carbonate (anhydrous), cover and fuse it by heating. After leaving it cooled, dissolve it with water and transfer it to a measuring flask of 1000 ml. Dilute it up to the marked line.
- (7) *p*-nitrophenol solution (0.2 W/v %)

7.3.3 Weighed Out Amount of Sample For the sample, 0.25 g shall be weighed out.

7.3.4 Operation The operation of determination shall be carried out according to the following procedures:

- (1) Weigh out the sample into a platinum crucible (for example, No. 30) (8). After mixing it with 2 g of sodium carbonate (anhydrous), cover it. At first heat it at a low temperature and fuse it by gradually raising the temperature. Successively heat it for 2 or 3 min.
- (2) After leaving it cooled, add about 5 ml of water to the platinum crucible and gently heat it. Crush the melt with a plastic bar and transfer the solution into a plastic beaker (100 ml). Repeat this operation until the melt is completely crushed.

- (3) Wash the platinum crucible and the cover with water and collect the filtrate into a plastic beaker (100 ml). After cooling, transfer it to a measuring flask of 100 ml and dilute it up to the marked line with water. Immediately thereafter, transfer it into a dry plastic beaker (200 ml).
- (4) Immediately thereafter, filter it by the use of a dry plastic beaker (100 ml), a dry plastic funnel and a dry filter paper (Class 5 C), and discard the initial filtrate of 10 to 20 ml. Accurately partially take a certain amount ⁽⁹⁾ of the filtrate to a plastic beaker (200 ml).
- (5) Add 2 or 3 drops of *p*-nitrophenol solution as an indicator. After dripping hydrochloric acid (1+1) until the colour of solution becomes colorless with mixing by shaking, dilute it to about 50 ml with water and add 1 ml of hydrochloric acid (1+4).
- (6) Add 4 ml of ammonium molybdate solution and mix it by shaking. Leave it as it is for 10 min. After adding 5 ml of tartaric acid, add 2 ml of ascorbic acid solution and mix by shaking. Transfer it into a measuring flask of 100 ml and dilute it up to the marked line with water. Leave it as it is for 30 min.
- (7) Take a part of this solution to the absorption cell of photometer and measure the absorbance near the wave length of 650 nm.

7.3.5 Calculation Obtain the amount of silicon dioxide from the calibration curve prepared in 7.3.6 and calculate the silicon dioxide content in sample from the following formula:

$$\text{Silicon dioxide (\%)} = \frac{a \times 10^{-3}}{W} \times \frac{100}{V} \times 100$$

where *a*: detected amount of silicon dioxide in
7.3.4 (7) (mg)

W: weighed out amount of sample (g)

V: partially taken amount in 7.3.4 (4) (ml)

7.3.6 Preparation of Calibration Curve Accurately dilute standard silicon dioxide solution 2 times with water and stepwise take 0 to 6.0 ml of it (0 to 0.3 mg as silicon dioxide) into a measuring flask of 100 ml. Dilute it to about 50 ml with water and 1 ml of hydrochloric acid (1+4) to each one of them. Thereafter, operate according to the procedures of 7.3.4 (6) and (7). Make the relation curve between the obtained absorbance and the silicon dioxide amount and allow this to be the calibration curve.

Notes ⁽⁸⁾ When the sample contains such reducing materials as organic substance, sulfides, etc., they shall be resolved by heating at 500 to 600°C.

⁽⁹⁾ The partially taken amount of filtrate shall be in accordance with Table 2 depending on the silicon dioxide content.

Table 2. Partially Taken Amount of Filtrate

Silicon dioxide content %	Partially taken amount ml
Less than 0.24	50
0.24 and over to 0.60 excl.	20
0.60 and over to 1.20 excl.	10

8. Iron (III) Oxide

8.1 Classification of Methods The method for determination of iron (III) oxide shall be in accordance with either of the following methods:

- (1) Absorptiometry of 1, 10-phenanthroline This method shall apply to the sample having the iron (III) oxide content of less than 1.50 %.
- (2) Atomic absorption method This method shall apply to the sample having the iron (III) oxide content of less than 1.00 %.

8.2 Absorptiometry of 1, 10-Phenanthroline

8.2.1 Summary Fuse the residuals in the platinum crucible stored in 7.2.4 with mixed fusing agent and dissolve it with hydrochloric acid. Let it become constant volume by adding it to the filtrate and washings stored in 7.2.4. Partially take a part of it, and reduce its iron with ascorbic acid. Add 1, 10-phenanthroline and colorate it by adjusting its pH with ammonium acetate. Measure its absorbance.

8.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1+1)
- (2) Mixed fusing agent For the mixed fusing agent, mix it by the weight ratio of [3 part of sodium carbonate (anhydrous) and 1 part of boric acid].
- (3) Ammonium acetate solution (20 W/v %)
- (4) Ascorbic acid solution (5 W/v %) For the ascorbic acid solution (5 W/v %), use the same one as that in 7.3.2 (5).
- (5) 1, 10-phenanthroline solution For the 1, 10-phenanthroline solution, dissolve 1 g of 1, 10-phenanthroline hydrochloride (1 hydrate) with water and dilute it to 1 l. Store it in a cold dark place. When it colours while stored, freshly prepare it.