

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical
Analysis of Metallurgical
Grade Fluorspar**

JIS M 8514—1989

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

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Methods for Chemical Analysis of
Metallurgical Grade Fluorspar

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1. Scope

This Japanese Industrial Standard specifies the methods for determination of calcium fluoride (¹), silicon dioxide (¹), calcium carbonate (¹), phosphorus, sulfur, arsenic, lead, and antimony in metallurgical grade fluorspar.

Note (¹) The calcium fluoride, silicon dioxide and calcium carbonate, respectively fluorine, silicon, and carbon dioxide are determined to be converted to each type.

2. Definitions

The definitions of principal terms used in this Standard shall be in accordance with JIS K 0050 and to others following definitions apply.

- (1) aliquot Accurate separation of solution by using a pipet.
- (2) to add V ml accurately Addition of V ml by using a buret or a pipet.
- (3) to add V ml Addition of V ml by using a meter glass or the like.
- (4) to add about V ml By putting, on trial, solution measured preliminarily with a graduated cylinder into an appliance to be used, a same amount is judged by the eye and is joined.
- (5) to analyze independently Analysis by changing one or all of man and the date.

3. General Matters

General matters common to the methods for chemical analysis shall be in accordance with the following Standards:

JIS K 0050 JIS K 0115 JIS K 0121 JIS Z 8401 JIS Z 8402

4. Sampling and Treating of Analytical Sample

4.1 Original Sample for Analysis Prepare a sample by sampling by a method specified between the delivery parties concerned, grind so that all thereof may pass through a standard sieve of 150 μ m (equivalent to 100 mesh), and take it as an original sample for analysis.

Applicable Standards and Corresponding International Standards: See page 31.

4.2 Sample for Analysis After sufficiently mixing an original sample for analysis, spread widely, thinly about 40 g thereof on a porcelain flat-bottom evaporating dish or the like, dry in an air bath at 105 to 110°C for 2 h, allow to stand to cool to room temperature in a desiccator, and take it as a sample for analysis.

4.3 Weighing of Sample For weighing out of an analytical sample, weigh out accurately an weighing out amount specified in each determination method from a sample for analysis to the nearest 0.1 mg by using a chemical balance.

5. Arrangement of Analytical Value

5.1 Number of Analyses Analyze, as a rule, a same sample two times independently.

5.2 Indication of Analytical Value Indicate an analytical value by mass percentage to the mass of a weighed out sample, and round off to the lowest place of indication specified according to an analytical component as follows in accordance with JIS Z 8401.

- (1) Components to be indicated to two places of decimals calcium fluoride, silicon dioxide, and calcium carbonate.
- (2) Components to be indicated to three places of decimals phosphorus, sulfur, arsenic, lead, and antimony.

5.3 Investigation of Analytical Value Investigate the accuracy and precision of an analytical value as follows:

- (1) Investigation of Accuracy When the absolute value of the difference between the average value of an analytical result ⁽²⁾ of a standard sample obtained by analyzing independently in parallel two times a kind of the standard sample of which chemical characteristic is similar to an analytical sample and a standard value, is less than a tolerance to the standard sample obtained from a standard deviation within the same laboratory indicated in each determination method by the formula (4.13) of 4.6.3 in JIS Z 8402, judge the accuracy of the analytical value obtained by simultaneous analysis to be satisfied.
- (2) Investigation of Analytical Precision in Same Laboratory When a range of two analytical results obtained by analyzing independently two times a same sample in a same laboratory is less than a tolerance within the same laboratory obtained from a standard deviation within the same laboratory indicated in each determination method in accordance with Table 1 of JIS Z 8402, judge the state to be no abnormal difference between those two analytical results.
- (3) Investigation of Analytical Precision between Different Laboratories In the case where results obtained by analyzing a same sample respectively independently two times in two different laboratories meet the condition of (2), when the absolute value of the difference between average values of respective two analytical results is less than a tolerance between different laboratories obtained from a standard deviation indicated in each determination

method in accordance with Table 1 of JIS Z 8402, judge the state to be no abnormal difference between analytical results in those two laboratories.

Note (2) When any abnormal value exists, discard in accordance with Procedure 2 (1) of 4.5 in JIS Z 8402.

5.4 Acceptance of Analytical Value Decide a final analytical value as follows:

- (1) As a result from investigation for two analytical results obtained by analyzing independently two times an object sample and for two analytical results to a kind of standard sample executed parallel thereto, when either of conditions of 5.3 (1) and 5.3 (2) are satisfied, judge the accuracy of analytical value and the analytical precision within the same laboratory to be no abnormality, and report the average value of two analytical results on the object sample to be a final value.
- (2) In the case where a parallel analysis on a standard sample is impossible, when the results of investigation for two analytical results on an object sample meet the condition of 5.3 (2), report the average value of those two analytical results to be a final value.
- (3) In the case where results of parallel analysis on a standard sample do not meet the condition of 5.3 (1), regard the accuracy of all results of analysis performed simultaneously therewith as doubtful, discard all the analytical results on the object sample as a rule, and analyze two times again.
- (4) In the case where two analytical results on an object sample do not meet the condition of 5.3 (2), regard either one or all of those analytical results as doubtful, discard all those analytical results as a rule, and analyze two times again.
- (5) In the case where two analytical results on an object sample do not meet the condition of 5.3 (2) and analysis is difficult to be performed again, treat according to 3.3.2 (1.2.2) of JIS Z 8402.

6. Method for Determination of Calcium Fluoride

6.1 Determination Method The method for determination of calcium fluoride shall be in accordance with evaporation thorium nitrate titrimetric method.

This method applies to the sample of all range in calcium fluoride content.

6.2 Evaporation Thorium Nitrate Titrimetric Method

6.2.1 Purport Add perchloric acid to a sample, perform steam distillation, and separate fluorine as hydrosilicofluoric acid. Regulate pH of the solution with a buffer solution, utilize Methylthymol Blue as an indicator, and titrate with thorium nitrate standard solution.

6.2.2 Reagents The reagents shall be as follows:

- (1) Perchloric acid (1.54 in specific gravity)
- (2) Buffer solution (3.5 in pH) Dissolve 94.5 g of monochloroacetic acid (CH_2ClCOOH) and 207.4 g of sodium monochloroacetate ($\text{CH}_2\text{ClCOONa}$) in water to 1 l.
- (3) Standard fluorine solution (10 mgF/ml) Weigh out 22.104 g of sodium fluoride (NaF) dried at 500°C to constant weight, dissolve in water, transfer to a 1000 ml one mark volumetric flask by using water, dilute to the mark with water, and take it as standard fluorine solution. Transfer this solution into a polyethylene bottle to be reserved.
- (4) 0.025 mol/l thorium nitrate standard solution Weigh out 13.803 g of thorium nitrate tetrahydrate $[\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}]$, dissolve in water, transfer to a 1000 ml one mark volumetric flask, and dilute to the mark with water. Standardize the factor of this solution as follows:

Weigh out accurately 50 ml of the solution obtained by diluting standard fluorine solution accurately 10 times into a beaker (300 ml), and add water to about 200 ml. After adding 5 ml of buffer solution of (2) thereto, utilize Methylthymol Blue solution as the indicator, titrate with 0.025 mol/l thorium nitrate standard solution, and calculate the factor (F) to 0.025 mol/l from the following formula:

$$F = \frac{V_1}{V_2 \times 1.900}$$

where V_1 : used amount of standard fluorine solution diluted 10 times (ml)

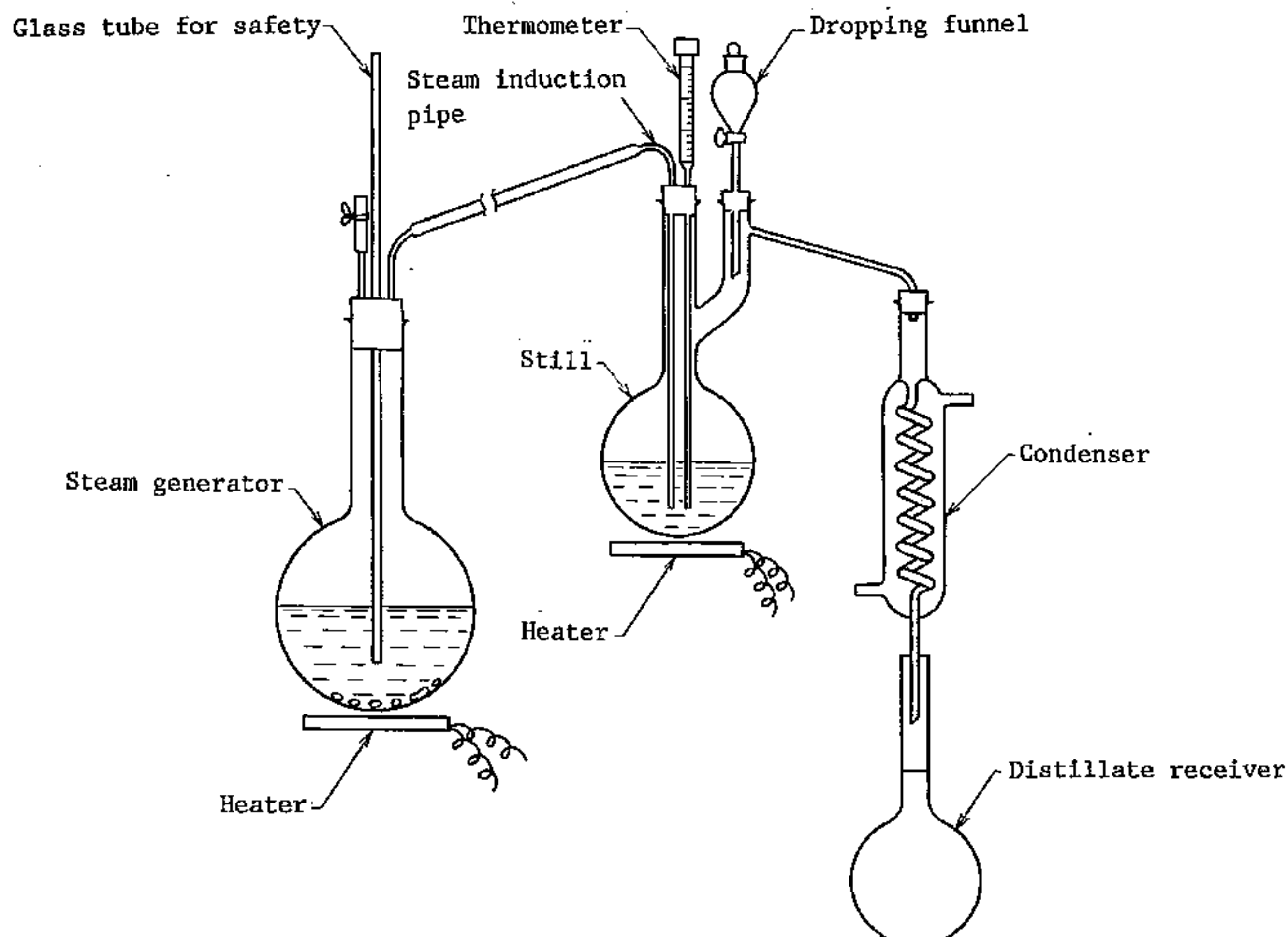
V_2 : used amount of 0.025 mol/l thorium nitrate standard solution (ml)

- (5) Methylthymol Blue solution (10 g/l)

6.2.3 Apparatus A fluorine distillation apparatus which is exemplified in Fig. 1 shall, as a rule, be used.

- (1) Steam Generator A round-bottom flask (3000 to 5000 ml) containing water and boiling chips.
- (2) Still A flask of 250 ml to a main pipe of which a steam induction pipe and a thermometer are attached and to a by pass of which a dropping funnel is attached.
- (3) Condenser A coiled condenser of 300 mm in length.
- (4) Heater

Fig. 1. Fluorine Distillation Apparatus (An Example)



6.2.4 Weighing out Amount of Sample The weighing out amount of a sample shall be 0.20 g.

6.2.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) **Distilling Separation** Weigh out a sample, transfer to a still by washing with a small amount of water, and add several boiling tips. Thereafter, further add 35 ml of perchloric acid. After passing cooling water through a condenser, heat the still. When a temperature inside the still has reached 140°C, introduce steam generated in a steam generator into the still ⁽³⁾. Continuously distill for 60 min at a speed of distillate of about 4 ml per minute. After ending distillation, wash the inside of the condenser with a small amount of water, and joint to the distillate.

Note ⁽³⁾ Preliminarily heat the steam generator to generate steam. However, do not introduce this steam into the still until a temperature inside the still reaches 140°C.

- (2) **Titration** Add 5 ml of buffer solution [6.2.2 (2)] to the solution obtained in (1), further add several drops of Methylthymol Blue solution as the indicator, titrate with 0.025 mol/l thorium nitrate standard solution, and take the point at which the solution turns blue as the end point.

6.2.6 Measurement of Distilling Efficiency The measurement of distilling efficiency shall, as a rule, be carried out according to the following procedures:

Transfer accurately 5 ml of standard fluorine solution to a still. After adding several boiling tips, further add 35 ml of perchloric acid. After passing cooling water through a condenser, heat the still. When a temperature in the still has reached 140°C, introduce steam generated in a steam generator into the still. Continue to distill at a speed of about 4 ml in distillate per minute for 60 min. After ending distillation, wash the inside of the condenser with a small amount of water, and joint to the distillate. Hereinafter operate following the procedure of 6.2.5 (2). Calculate distillation efficiency (R) from the following formula:

$$R = \frac{V \times F \times 1.900}{50}$$

where V : used amount of 0.025 mol/l thorium nitrate standard solution (ml)

F : factor of 6.2.2 (4)

6.2.7 Blank Test Carry out the whole operation of 6.2.5 without using a sample, and obtain a blank test value.

6.2.8 Calculation Calculate calcium fluoride content in a sample from the following formula:

$$\text{Calcium fluoride wt\%} = \frac{V \times F \times 0.003904}{m \times R} \times 100$$

where V : used amount of 0.025 mol/l thorium nitrate after correction of blank test value (ml)

F : factor of 6.2.2 (4)

m : weighing out amount of sample (g)

R : distillation efficiency

6.2.9 Analytical Precision The analytical precision by this method shall be as given in Table 1.

Table 1. Analytical Precision (⁴)

Unit: wt%	
Standard deviation within the same laboratory	Standard deviation between different laboratories
$0.0035 \times [\text{CaF}_2 \text{ (wt\%)}] + 0.1903$	$-0.0017 \times [\text{CaF}_2 \text{ (wt\%)}] + 0.9794$

Note (⁴) The analytical precision herein is obtained by using the sample of 75.24 wt% or over to and excluding 98.17 wt% in calcium fluoride content.

7. Method for Determination of Silicon Dioxide

7.1 Determination Method The method for determination of silicon dioxide shall be in accordance with molybdenum blue absorptiometry. This method applies to the sample of 0.2 wt% or over to and excluding 30 wt% in silicon dioxide content.

7.2 Molybdenum Blue Absorptiometry

7.2.1 Purport Fuse a sample with sodium carbonate, and dissolve the melt in warm water. Add basic acid, and regulate pH with hydrochloric acid. Thereafter, separately take a certain amount, and regulate pH with sulfuric acid, make silicic acid molybdosilicic acid with ammonium molybdate, allow tartaric acid to coexist with sulfuric acid, reduce it to molybdenum blue with ascorbic acid, and measure the absorbance.

7.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (10 + 7)
- (2) Sulfuric acid (1 + 1, 10 + 41)
- (3) Boric acid solution (40 g/l)
- (4) Sodium carbonate (anhydride)
- (5) Ammonium molybdate solution Dissolve 60 g of hexammonium heptamolybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ in water to 1 l. Filter this solution each service to be used.
- (6) Tartaric acid solution (100 g/l)
- (7) Ascorbic acid solution (20 g/l) Prepare each service.
- (8) Dilution solution Carry out the operation of 7.2.4 (1) by using only reagents, and take the obtained solution as dilution solution. Prepare this solution parallel to determination of a sample.
- (9) Standard silicon dioxide solution (150 μg SiO_2/ml) After heating silicon dioxide (SiO_2) (JIS K 8885) or quartz powder at 1000°C for 1 h, cool in desiccator. Weigh out 0.075 g of this cooled substance, transfer to a platinum crucible (No. 30), add 2.5 g of sodium carbonate (anhydride) to be mixed, cover the platinum crucible, heat initially at a low temperature, and fuse the contents. Thereafter, raise the temperature to 1000 to 1100°C, ignite for 15 min or over, and fuse thoroughly. Take the platinum crucible down from a heat source, and cool. Put together with the platinum crucible into a beaker (500 ml) containing 300 ml of warm water, dissolve the melt by quietly heating, wash the platinum crucible with water, and take it out. Transfer to a 500 ml one mark volumetric flask by using water, dilute to the mark with water, and take it as standard silicon dioxide solution. Transfer this solution to a polyethylene bottle to be reserved.

7.2.3 Weighing out Amount of Sample The weighing out amount of a sample shall be 0.20 g.

7.2.4 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) **Preparation of Sample Solution** Weigh out a sample, transfer to a platinum crucible (No. 30), add 4.0 g of sodium carbonate (anhydride) to be mixed, cover the platinum crucible, initially heat at a low temperature, and fuse the contents. Thereafter, raise temperature to 1000 to 1100°C, ignite for 10 min or over, and thoroughly fuse. Take the platinum crucible down from a heat source to be cooled. Put together with the platinum crucible into an ethylen tetrafluoride resin beaker (500 ml) containing 200 ml of warm water, quietly heat on a warm bath, and dissolve the melt. Wash the platinum crucible with water, and take it out. After cooling the solution to room temperature, dilute to 300 ml with water, add 20 ml of boric acid solution, add accurately, quietly 12 ml of hydrochloric acid (10 + 7), and sufficiently mix ⁽⁵⁾. Cover with a watch glass, quietly heat, and boil for 3 min. Thereafter, take it down from the heat source, cool to ordinary temperature, transfer to a 500 ml one mark volumetric flask by using water, and dilute to the mark with water.

Note ⁽⁵⁾ pH of the solution at that time has become 2.0.

- (2) **Coloration** Separately take a portion of the solution obtained in (1) following Table 2, transfer to a 100 ml one mark volumetric flask, add accurately dilution solution [7.2.2 (8)] according to the aliquot amount following Table 2, and add 40 ml of water to 60 ml in total amount. Add accurately 1 ml of sulfuric acid (10 + 41) to be sufficiently mixed ⁽⁶⁾.

Add 10 ml of ammonium molybdate [7.2.2 (5)], mix by shaking, and allow to stand for 15 min. Then add 5 ml of tartaric acid solution, mix by shaking, and allow to stand for 5 min. Then, add continuously, quickly 10 ml of sulfuric acid (1 + 1) and 2 ml of ascorbic acid solution with mixing by shaking, and dilute to the mark with water.

Table 2. Aliquot Amount

Silicon dioxide content wt%	Aliquot amount ml	Dilution solution additional amount ml
0.2 or over to and excl. 6	20	0
6 or over to and excl. 12	10	10
12 or over to and excl. 30	5	15

Note ⁽⁶⁾ pH of the solution at that time has become 1.1.

- (3) **Measurement of Absorbance** After leaving the coloration solution obtained in (2) as it is for 30 min, take a portion thereof into an absorption cell (10 mm, made of glass), take water as contrast matter, and measure the absorbance near 650 nm in wavelength

7.2.5 Blank Test Separately take 20 ml of dilution solution [7.2.2 (8)], transfer to a 100 ml one mark volumetric flask, and add 40 ml of water to 60 ml in total amount. Hereinafter, operate following the procedures on and after the addition of 1 ml of sulfuric acid (10 + 41) of 7.2.4 (2), and obtain the absorbance of blank test.

7.2.6 Preparation of Working Curve The working curve shall be prepared as follows:

Separately take stepwise 0 to 4 ml of standard silicon dioxide solution (0 to 600 μg as silicon dioxide) into five beakers (200 ml). Add accurately 20 ml of dilution solution [7.2.2 (8)], and regulate pH at 2.0 by using hydrochloric acid (10 + 7).

Transfer to a 100 ml one mark volumetric flask by using water. After diluting total amount to 60 ml with water, operate following the procedures on and after the addition of 1 ml of sulfuric acid (10 + 41) of 7.2.4 (2), obtain the relation between the obtained absorbance and the amount of silicon dioxide in the coloration solution, and take it as the working curve.

7.2.7 Calculation Obtain the amount of silicon dioxide by inserting the absorbance after correcting the blank test value obtained by subtracting the absorbance obtained in 7.2.5 from the absorbance obtained in 7.2.4 into the working curve prepared in 7.2.6, and calculate the content of silicon dioxide in a sample from the following formula:

$$\text{Silicon dioxide wt\%} = \frac{A}{m \times B} \times 100$$

where A : detection amount of silicon dioxide in aliquot sample solution (g)

m : weighing out amount of sample (g)

B : aliquot ratio of sample solution

7.2.8 Analytical Precision The analytical precision by this method shall be as given in Table 3.

Table 3. Analytical Precision (⁷)

Unit: wt%	
Standard deviation within same laboratory	Standard deviation between different laboratories
$0.0038 \times [\text{SiO}_2 \text{ (wt\%)}] + 0.0269$	$0.0062 \times [\text{SiO}_2 \text{ (wt\%)}] + 0.0398$

Note (⁷) The analytical precision herein is obtained by using the sample of 1.45 wt% or over to and excluding 21.16 wt% in silicon dioxide content.

8. Method for Determination of Calcium Carbonate

8.1 Determination Method The method for determination of calcium carbonate shall be in accordance with carbon dioxide-barium hydroxide absorption neutralization titrimetric method. This method applies to the sample of 0.1 wt% or over to and excluding 10 wt% in calcium carbonate content.