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Method for chemical analysis of ferromolybdenum

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law. Consequently **JIS G 1317:1982** is replaced with **JIS G 1317:1998**.

In this revision, **ISO 4173** has been employed in Annex 2 for conforming to International Standards, and determinations of each component are specified in Annexes 1 to 14.

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Method for chemical analysis of ferromolybdenum

Introduction In the application of standard, normative references to the standard shall be simultaneously referred to. Since ferromolybdenum has many chances to be used as the supplementary raw material in iron and steel making process, JIS G 1317, which specifies the determination of molybdenum as main element and other 6 elements containing carbon which give rise to discussion in the iron and steel production, was established in 1953. Annex 2 is the Japanese Industrial Standard prepared based on ISO 4173 *Ferromolybdenum—Determination of molybdenum content—Gravimetric method*, published in 1980 as the first edition, without modifying technical contents.

The “Informative reference” underlined with dots in Annex 2 shows the matters not given in the original International Standard.

1 Scope This Standard specifies the methods for determination of molybdenum, carbon, silicon, phosphorus, sulfur, copper and aluminum in ferromolybdenum.

2 Normative references The following standards contain provisions which, through reference in this standard, constitute provisions of this Standard. The most recent editions of the standards indicated below shall be applied.

JIS G 1301 *General rules for chemical analysis of ferroalloys*

JIS K 0116 *General rules for atomic emission spectrometry*

JIS K 0121 *General rules for atomic absorption spectrochemical analysis*

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

JIS Z 2615 *General rules for determination of carbon in metallic materials*

JIS Z 2616 *General rules for determination of sulfur in metallic materials*

JIS Z 8402 *General rules for permissible tolerance of chemical analyses and physical tests*

3 General matters General matters common to the methods for chemical analysis shall be in accordance with JIS G 1301, JIS K 0116 and JIS K 0121. However, these shall not be applied to Annex 2.

4 Classification of the method for determination The methods for determination of each component in ferromolybdenum shall be according to Table 1.

Table 1 The methods for determination of each component in ferromolybdenum

Component	Determination method	Range of percentage of components % (m/m)	Annex (normative) No.
Molybdenum	Iron separation zinc amalgam reduction potassium permanganate titration method	50 or over up to and incl. 80	1
	8-quinolinol molybdenum gravimetric method (ISO 4173)	50 or over up to and incl. 80	2
Carbon	Combustion-gas volumetric method	0.05 or over up to and incl. 6.0	3
	Combustion-infrared absorption method	0.001 or over up to and incl. 6.0	4
Silicon	Silicon dioxide gravimetric method	0.05 or over up to and incl. 3.0	5
	ICP emission spectrochemical method	0.02 or over up to and incl. 1.0	6
Phosphorous	Beryllium hydroxide coprecipitation separation phosphomolybdenum blue absorptiometric method	0.002 or over up to and incl. 0.10	7
	Beryllium hydroxide coprecipitation separation ICP emission spectrochemical method	0.002 or over up to and incl. 0.10	8
Sulfur	Combustion-potassium iodate titration method	0.005 or over up to and incl. 0.20	9
	Combustion-infrared absorption method	0.001 or over up to and incl. 0.20	10
Copper	Atomic absorption method	0.01 or over up to and incl. 0.50	11
	ICP emission spectrochemical method	0.01 or over up to and incl. 0.50	12
Aluminium	Atomic absorption method	0.005 or over up to and incl. 0.20	13
	ICP emission spectrochemical method	0.005 or over up to and incl. 0.20	14

Annex 1 (normative)**Determination of molybdenum — Iron separation zinc amalgam reduction
potassium permanganate titration method**

1 Summary A sample is decomposed with sulfuric acid and nitric acid, concentrated by heating. Remove nitric acid by generation of white fumes of sulfuric acid, and separate iron, etc. as hydroxide with sodium hydroxide. Concentration of acid is adjusted with sulfuric acid, add zinc amalgam and mix by shaking. After reducing molybdenum, it is titrated with potassium permanganate standard solution.

2 Reagents The reagents shall be as follows :

- a) **Nitric acid (1+1)**
- b) **Sulfuric acid (1+1)**
- c) **Carbon dioxide**
- d) **Fusing mixture [sodium carbonate 1 part and potassium carbonate 1 part]**
- e) **Zinc amalgam** 450 g of mercury is transferred into an Erlenmeyer flask (300 ml), added with 10 g of granular zinc, from which oxide film on the surface is removed with sulfuric acid (1+10), and its surface is covered with small amount of sulfuric acid (1+10). The granular zinc is dissolved by heating on water bath with occasional shaking, cooled to room temperature and the surface of amalgam is covered with small amount of sulfuric acid (1+10) to be stored.

WARNING FOR SAFETY As zinc amalgam is heavily poisonous, this reagent and a solution with this reagent added shall be handled with care.

- f) **Sodium hydroxide solution (200 g/l)**
- g) **Ammonium iron (III) sulfate solution** Dissolve 100 g of ammonium iron (III) sulfate 12 hydrate in water, add little by little 50 ml of sulfuric acid (1+1) and 400 ml of phosphoric acid under mixing it by shaking, and dilute to 1 000 ml with water.
- h) **0.02 mol/l potassium permanganate standard solution** The method for preparation and standardization shall be in accordance with 4.5 (7) of JIS K 8001.

3 Apparatus The reduction apparatus shown in Attached Fig. 1 of Annex 1 shall, as a rule, be used. The part below the lower cock shall be filled with water which is boiled to remove air and cooled.

4 Test portion Weigh out 0.50 g to the nearest 0.1 mg.

5 Operation

5.1 Decomposition of sample The decomposition of a sample shall be carried out according to the following procedures.

- a) Weigh out a sample and transfer it to a beaker (300 ml) and cover it with a watch glass.
- b) Add 20 ml of sulfuric acid (1+1) and 5 ml of nitric acid (1+1), and decompose it by

heating.

- c) After allowing it to cool, wash the bottom side of the watch glass, remove it and heat the beaker until white fumes of sulfuric acid start to be generated.
- d) Expel nitric acid thoroughly by further heating for (15 to 20) minutes under generating white fumes of sulfuric acid.
- e) After allowing it to cool, add about 100 ml of warm water and dissolve soluble salts by heating ⁽¹⁾.
- f) Filter it through a filter paper (Class 5B), wash it with warm water, receive the filtrate and the washings with a beaker (300 ml) and reserve it as a main solution.

Transfer the residue and filter paper into a nickel crucible (No.30), incinerate the filter paper at 600 °C max. Then add fusing mixture [2 d)] about 10 times amount of the residue and dissolve by heating. After allowing it to cool, dissolve the melt in water and compound it into main solution.

Note ⁽¹⁾ In case of absence of insoluble residue, the following operation f) shall not be carried out.

5.2 Separation of iron, etc. Separation of iron, etc. shall be carried out according to the following procedure.

- a) Add little by little sodium hydroxide solution to the solution obtained in 5.1 e) or f) with stirring, neutralize it until the precipitate of iron (III) hydroxide is slightly produced and further add 20 ml of it in excess.
- b) After boiling it for (3 to 5) minutes by gentle heating, cool it to ordinary temperature, transfer it into a volumetric flask of 250 ml by adding water and dilute it with water up to the marked line.
- c) Filter the solution into a dry beaker (300 ml) through a dry filter paper (Class 5B).
- d) Discard the initial filtrate, take separately 50 ml from the subsequent filtrate and transfer it into a beaker (100 ml).

5.3 Reduction of molybdenum Reduction of molybdenum shall be carried out according to the following procedure.

- a) Add 6 ml of sulfuric acid (1+1) to the solution which is separately taken in 5.2 d) and stir it.
- b) Transfer the solution into reduction apparatus of 3 with about 200 g of zinc amalgam [2 e)] in it by washing with a small amount of water ⁽²⁾.
- c) After substituting air by passing carbon dioxide for about 3 minutes, mix them by violently shaking for about 5 minutes and reduce molybdenum thoroughly.

Note ⁽²⁾ As the concentration of sulfuric acid at reduction operation, approximately 0.75 mol/l should be suitable, so the amount of water for transferring shall be smaller than 15 ml.

5.4 Titration Carefully and thoroughly transfer the zinc amalgam in a reduction apparatus to the receiver, titrate it immediately with 0.02 mol/l potassium permanganate standard

solution [2 h)], taking care that the air does not enter the reduction apparatus (³) (⁴), and take the point at which color of solution turns to faint red as the end point.

Notes(³) When the reduction apparatus shown in Attached Fig. 1 (b) in Annex 1 is used, it shall be titrated with passing carbon dioxide.

(⁴) As the reduced molybdenum is relatively easy to be oxidized, it shall be carefully operated so that the solution does not touch the air after reduction of molybdenum.

Further, in order to prevent oxidation of molybdenum, the following may be carried out : reduce molybdenum and remove zinc amalgam from the solution, add ammonium iron (III) sulfate solution [2 g)] and oxidize molybdenum, and titrate the reduced iron (II).

6 Blank Test Blank test shall not be carried out.

7 Calculation The content of molybdenum in sample shall be calculated from the following formula.

$$Mo = \frac{V \times F \times 0.003\,198}{m \times \frac{1}{5}} \times 100$$

where *Mo* : content of molybdenum in the sample [% (m/m)]

V : titration volume of 0.02 mol/l potassium permanganate standard solution obtained in 5.4 (ml)

F : factor of 0.02 mol/l potassium permanganate standard solution

m : test portion (g)

8 Tolerance Tolerance (⁵) shall be in accordance with Table 1 of Annex 1.

Annex 1 Table 1 Tolerance

Unit : % (m/m)

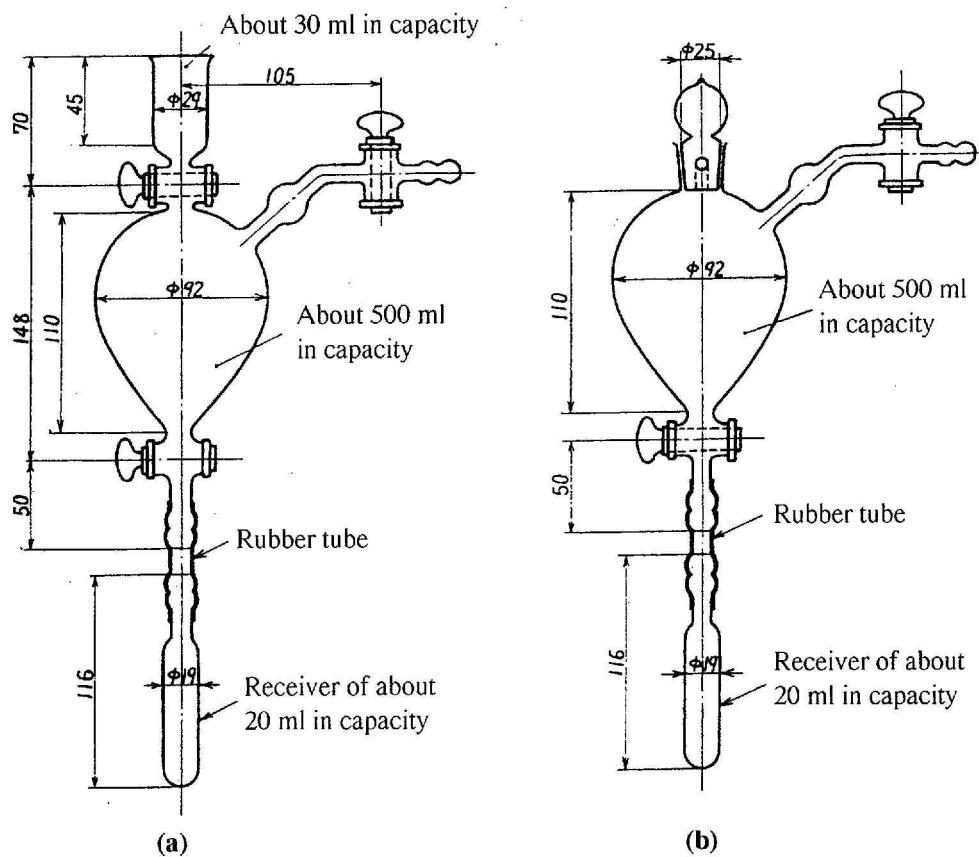
Alloy type	Tolerance of reproducibility within laboratory	Tolerance of reproducibility between laboratories
Low carbon ferromolybdenum	<i>D</i> (<i>n</i>) [0.14]	<i>D</i> (<i>n</i>) [0.18]
High carbon ferromolybdenum	<i>D</i> (<i>n</i>) [0.15]	<i>D</i> (<i>n</i>) [0.32]

Note (⁵) *D*(*n*) in calculation formula of tolerance means *D*(*n*, 0.95) and this value is according to Table 4 of JIS Z 8402. The *n*-value in tolerance of reproducibility within laboratory means the number of analyses in the same test laboratory and that in tolerance of reproducibility between laboratories means the number of test laboratories which carried out the analysis.

Informative reference : These tolerances are determined by the results of cooperation test using low carbon ferromolybdenum of 60.8 % (m/m) molybdenum and high carbon ferromolybdenum of 60.4 % (m/m) molybdenum.

6
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Unit : mm



Annex 1 Attached Fig. 1 Reduction apparatus

Annex 2 (normative)
Determination of molybdenum — 8-quinolinol
molybdate gravimetric method (ISO 4173)

1 Scope This Annex 2 specifies the method for determination of molybdenum in ferromolybdenum by 8-quinolinol molybdate gravimetric method.

This method shall be applied to ferromolybdenum in which molybdenum content is 50 % (m/m) or over up to and including 80 % (m/m).

Informative reference 1 In the original Standard, the name of this method is described as only “gravimetric method”. However, in this Standard, it is stated as “8-quinolinol molybdate gravimetric method” in accordance with the name of determination method in JIS.

The name of reagent in the original ISO Standard is described as “8-hydroxyquinoline”, but in this Standard “8-quinolinol” is used in accordance with nomenclature of IUPAC.

2 In the original ISO Standard, it is said as “molybdenum contents in the range normally found in ferromolybdenum”, but definite figures are given in this Standard in accordance with ranges of concentration of molybdenum specified in ferromolybdenum specification.

2 Normative references

ISO 3713 *Ferroalloys—Sampling and preparation of samples—General rules* [foot-note¹⁾]

Informative reference : In the original ISO Standard, the footnote says “At present at the stage of draft”, but this Standard was published in 1987.

3 Principle Dissolve the test portion, and separate iron with sodium hydroxide. Precipitate the molybdenum as the 8-quinolinol salt in the presence of ethylene diamine tetraacetate dihydrogen disodium dihydrate (hereafter referred to as EDTA2Na) and ammonium oxalate. Filtrate, dry and weigh anhydrous 8-quinolinol molybdate [$\text{MoO}_2(\text{C}_8\text{H}_6\text{NO})_2$].

4 Reagents During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sulfuric acid 50 % (V/V) solution Add little by little 500 ml of sulfuric acid (ρ 1.84 g/ml) into 400 ml of water with cooling. Cool it with stirring and dilute the volume to 1 000 ml with water.

4.2 Nitric acid 25 % (V/V) solution Dilute 250 ml of nitric acid (ρ 1.42 g/ml) to 1 000 ml with water.

4.3 Hydrofluoric acid (ρ 1.14 g/ml)

4.4 Hydrochloric acid 50 % (V/V) solution Add water into 500 ml of hydrochloric acid (ρ 1.16 g/ml to 1.18 g/ml) and dilute the volume to 1 000 ml with water.

4.5 Sodium hydroxide solution (460 g/l to 480 g/l) Weighing (460 to 480) g of sodium hydroxide, put it into a polyethylene beaker. Dissolve sodium hydroxide in water by cooling the outside wall of the beaker with flowing water and dilute to 1 000 ml and mix. This solution shall be stored in a polyethylene bottle.

4.6 EDTA2Na solution (10 g/l) Dissolve 10 g of EDTA2Na into water and dilute to 1 000 ml.

4.7 Ammonia solution 50 % (V/V) Add water into 500 ml of ammonia solution (ρ 0.91 g/ml) and dilute the volume to 1 000 ml.

4.8 8-quinolinol solution (30 g/l) neutral solution Dissolve 3 g of 8-quinolinol in 12 ml of acetic acid, add 60 ml of water and warm to about 40 °C. Add the ammonia solution (4.7) dropwise until a slight permanent precipitate is formed. Dissolve again the precipitate by adding dropwise acetic acid with care, cool and dilute to 100 ml with water.

4.9 Nitric acid ρ 1.42 g/ml

4.10 Hydrochloric acid ρ 1.16 g/ml to 1.18 g/ml

4.11 Ammonium oxalate

5 Apparatus Use the usual apparatus and equipment in an analysis laboratory.

6 Sample Use powder sample which will pass through a sieve with a mesh size of 160 μm , prepared in accordance with ISO 3713.

7 Operation

7.1 Test Portion Owing to the inhomogeneity of ferromolybdenum, the sample which has been passed through a screen of mesh opening 160 μm should be sieved again with a screen of mesh opening 75 μm to 80 μm and proportionate parts of over- and under-size used for analysis.

Weigh out 1 g for 75 % (m/m) ferromolybdenum or 1.25 g for 50 % (m/m) ferromolybdenum.

7.2 Determination Take the test portion (7.1) in a polytetrafluoroethylene (PTFE) beaker (150 ml), add 10 ml of sulfuric acid solution (4.1) and warm without boiling. Add, dropwise, the nitric acid (4.9) until the test portion is dissolved and then add 0.5 ml in excess. Add 5 ml of the hydrofluoric acid (4.3) and evaporate until fumes of sulfur trioxide are evolved. Continue fuming for 15 minutes, cool, add 5 ml each of hydrochloric acid (4.10) and nitric acid (4.9), warm for 10 minutes and dilute to about 50 ml.

Into a tall beaker (capacity 650 ml to 800 ml), take 50 ml of the sodium hydroxide solution (4.5) and 50 ml of water. Heat to boil and place a funnel in a mouth of the beaker.

Note : It is desirable to use the funnel which has been made by drawing out the stem of a 75 ml funnel to produce a jet size of diameter approximately 1 mm.

Transfer the test solution slowly, through the funnel, into the beaker containing boiling sodium hydroxide solution. Rinse the PTFE beaker with hot water (85 °C to 90 °C) and transfer the washings to the funnel. Rinse the funnel and upper surface of the tall beaker, boil the solution for 2 to 3 minutes, dilute to about 450 ml and cool.

Transfer to 500 ml of one mark volumetric flask, and dilute to the mark with water. Dry the original tall beaker, transfer the solution of the volumetric flask into it and allow to stand for 15 to 20 minutes.

Filter a portion of the solution through a dry, rapid-hardened filter paper and transfer a 100 ml aliquot to a beaker (400 ml). Dilute it to about 200 ml with water and add 10 ml of the EDTA2Na solution (4.6) and 3 g of the ammonium oxalate (4.11). Warm gently to dissolve the ammonium oxalate, cool to room temperature and adjust the solution to pH 4.0 using a pH meter by addition of the hydrochloric acid (4.4) and the ammonia solution (4.7).

Heat the solution to boiling and add 20 ml of the 8-quinolinol solution (4.8), ensuring that the solution continues to boil throughout the addition.

Note : It is essential that the precipitation be carried out in a boiling solution. If precipitation is carried out in a solution below boiling point, the precipitate formed is more difficult to wash and initially gives high recoveries ; if dried until constant mass (perhaps 2 to 3 days) is reached, low recoveries may sometimes be obtained.

Allow to stand for 5 to 10 minutes at 80 °C to 90 °C with occasional stirring and filter through a sintered glass filter (porous 5 µm to 10 µm) with a known mass (this mass shall be m_2), by using gentle suction. Remove the precipitate from the walls of beaker with using a glass rod with rubber, transfer it to the glass filter and wash the precipitate in the filter with about 100 ml of hot water (80 °C to 90 °C).

Informative reference : As it is difficult to understand the description in the original text, this writing was added.

Note : During filtration, it is needed that not more than half of the filter should be filled with the solution at any time. This procedure facilitates the efficient washing of the filter and provides a precipitate free from soluble salts.

Dry overnight at 125 °C, cool and weigh. Re-dry to constant mass and weigh as anhydrous 8-quinolinol molybdate (this mass shall be m_1).

Informative reference : As it is difficult to understand the description in the original text, this writing was added.

Note : The following procedures are recommended for handling and cooling a sintered glass filter.

- a) After washing with suction, the outside wall of the filter should be washed with hot water, dried on a filter paper and, from that stage, should not be touched with bare hands. The filters (or crucibles) should preferably be handled with tweezers or for a minimum period in a gloved hand.
- b) After drying in an oven, both the empty filters and those containing the 8-quinolinolate precipitates should be placed in an efficient desiccator and allowed to stand at room

temperature for 1 hour before weighing.

- c) Before use, the filters should be washed several times with hot water, nitric acid solution (4.2) and finally with water and dried at 125 °C. Cool in an efficient desiccator to room temperature and use this filter as a filter of which the mass is known after confirming the constant mass.

Informative reference : In order to make it easy to understand the meaning of the filter of which the mass is known, this writing was added.

Transfer the used filter in a small beaker containing 5 ml to 10 ml of sulfuric acid solution (4.1) after removing the bulk of the precipitate with a jet of water and fill it with nitric acid (4.9). Heat the beaker until fumes of sulfuric acid are generated, and cool it. Remove the filter from the beaker and pass about 100 ml of hot water through the filter under gentle suction. Carry out the washed filter as in a) and b) above.

8 Expression of results The molybdenum content [% (m/m)] is calculated by the following formula.

$$\frac{(m_1 - m_2) \times 23.05}{m_0}$$

where m_1 : the mass of the glass filter containing the anhydrous 8-quinolinol molybdate (g)

m_2 : the mass of the used glass filter (g) [Note : Refer to c)]

m_0 : the mass of the test portion in the final aliquot solution (g)

Remarks : As it is difficult to understand the description in the original text, this writing was added.

9 Reproducibility A cooperated test of this method was carried out by different seven laboratories. The tests of five times for each of two samples were carried out by each analyst. From the results obtained, the 95 % confidence limits (2s) given in the table have been calculated.

Table Reproducibility according to alloy types

Alloy type	Molybdenum content % (m/m)	Standard deviation		Tolerance of reproducibility between laboratories index 2s
		s_b	s_w	
50 % (m/m) Ferromolybdenum	50.33	0.081	0.090	0.24
75 % (m/m) Ferromolybdenum	75.34	0.085	0.100	0.26

10 Test report The following particulars shall be included in a test report.

- The items in accordance with this Annex
- The items on identification of sample

- c) The results of analysis
- d) Any unusual features noted during the determination
- e) The detailed items of any operation unspecified in this Annex or optional operation

Annex 3 (normative)**Determination of carbon — Combustion-gas volumetric method**

1 Summary Heat a sample in an oxygen gas flow at a high temperature, oxidize carbon to carbon dioxide. Collect it together with oxygen into a burette, measure the volume of gas. Then let an alkali solution absorb carbon dioxide to be removed, and measure the volume of remaining gas.

2 Apparatus The apparatus shall be in accordance with 6.3.2 of 6.3 in JIS Z 2615.

3 Equipment and materials The equipment and materials shall be in accordance with 5 in JIS Z 2615.

4 Test portion and additional weight of accelerator Weigh out the sample, to the nearest 0.1 mg, according to Annex 3 Table 1:

Annex 3 Table 1 Test portion

Carbon contents % (m/m)	Test portion g
0.01 or over to and excl. 0.1	2.0
0.1 or over to and excl. 1.0	1.0
1.0 or over to and excl. 3.0	0.50
3.0 or over up to and incl. 6.0	0.25

5 Operation

WARNING FOR SAFETY In the combustion process, it shall be taken care that a pair of tongs for a crucible shall always be used in handling of a porcelain combustion boat heated at a high temperature or a combustion crucible for fear that the skin or fingers of an operator may be burnt.

And efforts shall be made to prevent occurrence of a fire by paying attention to the treatment of excessive exhaust oxygen gas.

5.1 Preparation for operation The preparation for operation shall be in accordance with 6.3.3 of 6.3 in JIS Z 2615.

When a tubular electric resistance heating furnace is used, a temperature in the combustion tube shall be kept at 1 300 °C. to 1 400 °C (¹).

When a high frequency induction heating furnace is used, the conditions for high frequency induction heating shall be established (²).

Notes(¹) Correct the temperature paying regard to the differences between the temperature of the inside combustion tube and that of thermometer indication.

- (²) For example, the parameter, such as anodic current of high frequency oscillator and grid current which are depending on the specification of the applied equipment.

5.2 Determination The determination shall be carried out in accordance with either one of the following procedures (³). Attached Fig. 2 (No.1) in **JIS Z 2615** shall be referred to in each case.

Note (³) In the daily works, the apparatus and equipment shall be tested whether they are controlled to satisfy the performance criteria or not, at the beginning, the middle, and the end of a working time, in accordance with the same procedures as the determination of the analytical sample, by using the samples with known carbon contents.

a) When a tubular electric resistance heating furnace is used

- 1) Weigh out the sample and transfer it into the porcelain combustion boat (⁴).
- 2) Open the inlet of the combustion tube of the tubular electric resistance heating furnace and insert the porcelain combustion boat containing the sample into the combustion tube and place it in the center of the tube. Immediately, stopper it airtightly.
- 3) Turn a three way stopcock f) to the furnace side and allow to stand for 2 min, while adjusting the flow of oxygen.
- 4) Hereafter, carry out the procedures in accordance with 6.3.4 2) to 6) of 6.3 in **JIS Z 2615**.

Note (⁴) Select the most adequate accelerator (for example iron, tin, tungsten, etc.) which is listed in the 5 (13) in **JIS Z 2615**, and add the optimum amount of accelerator for the applied apparatus or equipment. Mix the accelerator added thoroughly with the sample.

b) When a high frequency induction heating furnace is used

- 1) Weigh out the sample and transfer into the porcelain combustion crucible (⁴).
- 2) After connecting the apparatus and confirming the airtightness, close the three way stopcock (m), and open the three way stopcock (l) to the open air side.
- 3) Place the porcelain combustion crucible containing the sample obtained in 1) operation on a bearer of high frequency induction heating furnace, insert the crucible to the center of the heating coil with operating the handle and close the combustion tube.
- 4) Flow oxygen into the combustion tube and replace the air with oxygen.
- 5) Close the three way stopcock (l) and start to work the high frequency induction heating furnace.
- 6) Open the three way stopcock (m) to the furnace side after passing (10 to 20) s. Then open the three way stopcock (l) slightly to the furnace side and introduce the combustion gas into the burette (n) through the desulfurization tube (j) and the cooling tube (k).
- 7) After almost finishing the combustion of the sample which takes about 1 min, collect the mixed gas rapidly close to the bottom graduation of the burette (n).
- 8) Close the three way stopcocks (l) and (m). Allow to stand still for about 1 min after

stopping the high frequency induction heating.

- 9) Hereafter, carry out the procedures in accordance with (4) to (6) of 6.3.4 of 6.3 in JIS Z 2615.

6 Blank test The blank test shall be carried out in accordance with 6.3.5 of 6.3 in JIS Z 2615. However, when a high frequency induction heating furnace is used, in which the porcelain combustion crucible without sample does not induce the current, carry out the blank test with the steel sample of which amount is the same as the sample and the carbon content is as low as possible and known. The blank test value of carbon shall be determined by subtracting the known carbon contents in the steel sample used for the blank test from the carbon contents obtained by the blank test.

7 Calculation The calculation shall be in accordance with 6.3.6 of 6.3 in JIS Z 2615.

Annex 4 (normative)
Determination of carbon — Combustion-infrared absorption method

1 Summary Heat a sample in a oxygen gas flow at a high temperature, oxidize carbon to carbon dioxide and carbon monoxide. Send this gas together with oxygen to the infrared absorption cell, and measure the infrared absorption amounts of carbon dioxide and carbon monoxide.

2 Apparatus Apparatus shall be in accordance with 6.9 or 6.10 in JIS Z 2615. A tubular electric resistance heating furnace may be also used for sample combustion parts of the integration method.

3 Equipment and materials Equipment and Materials shall be in accordance with 5 in JIS Z 2615.

4 Test portion Weigh out the optimum mass of the sample, to the nearest 0.1 mg, depending on the specification of the apparatus used.

Remarks : Test portion of the sample is 0.50 g or 1.0 g in general.

5 Operation

WARNING FOR SAFETY In the combustion process, it shall be taken care that a pair of tongs for a crucible shall always be used in handling of a porcelain combustion boat heated at a high temperature or a combustion crucible for fear that the skin or fingers of an operator may be burnt.

And efforts shall be made to prevent occurrence of a fire by paying attention to the treatment of excessive exhaust oxygen gas.

5.1 Preparation for operation The preparatory operation shall be in accordance with preliminary procedures of 6.9 or 6.10 in JIS Z 2615. In case of using a tubular electric resistance heating furnace, the temperature in the combustion tube shall be kept at 1 200 °C to 1 300 °C.

5.2 Determination The determination shall be carried out in accordance with any one of the following procedures (1).

Note (1) In the daily works, the apparatus and equipment shall be tested whether they are controlled to satisfy the performance criteria or not, at the beginning, the middle, and the end of a working time, in accordance with the same procedures as the determination of the analytical sample, by using the samples with known carbon contents.

a) **When the integration method with a tubular electric resistance heating furnace is employed**

1) Weigh out the sample and transfer it into the porcelain combustion boat.

- 2) Weigh correctly 1 g to 2 g of the accelerator ⁽²⁾ and put it on the sample in a porcelain combustion boat of 1).
 - 3) Open the inlet of the combustion tube of the tubular electric resistance heating furnace and insert the porcelain combustion boat containing the sample and the accelerator into the tube and place it in the adequate position of the combustion tube. Immediately stopper it airtightly.
 - 4) Blow the optimum volume of oxygen and introduce the generated gases with oxygen into the infrared detector.
 - 5) Read out the indicated value for the integral values of infrared absorption amount which is corresponding to the contents of carbon dioxide and carbon monoxide in the generated combustion gas.
- b) **When the integration method with a high frequency induction heating furnace is employed**
- 1) Weigh out the sample and transfer it into the porcelain combustion crucible.
 - 2) Weigh correctly 1 g to 2 g of the accelerator ⁽³⁾ and put it on the sample in the porcelain combustion crucible of 1).
 - 3) Place the porcelain combustion crucible containing the sample and accelerator on a bearer of high frequency induction heating furnace, insert the crucible to the center of the heating coil with operating the handle and close the combustion tube.
 - 4) Hereafter, carry out the procedures in accordance with (2) to (3) of 6.9.5 of 6.9 in JIS Z 2615.
- c) **When the circulating method with a high frequency induction heating furnace is employed** Determination with the circulating method shall be carried out in accordance with the procedures of 6.10.4 of 6.10 in JIS Z 2615.

Notes⁽²⁾ It is better to use copper or tin as the accelerator. The optimum amounts shall be prepared according to the specification of apparatus used.

⁽³⁾ It is better to use the mixture of the equivalent weight of tungsten and tin or copper. The optimum amounts of it shall be prepared according to the specification of apparatus used.

6 Blank test Carry out the blank test with using only the accelerator of the same mass as the analysis of the sample, in parallel with the same procedures of the sample.

7 Calculation Calculation shall be carried out in accordance with 6.9.7 of 6.9 or 6.10.6 of 6.10 in JIS Z 2615.

Annex 5 (normative)
Determination of silicon — Silicon dioxide gravimetric method

1 Summary Decompose a sample with nitric acid and hydrochloric acid, add sulfuric acid and heat, convert silicon to insoluble silicon by generating white fumes of sulfuric acid. After filtrating it, ignite the precipitate to attain a constant weight and weigh the mass. Add sulfuric acid and hydrochloric acid, heat silicon dioxide to evaporate as silicon tetrafluoride. After igniting the residue to attain a constant weight, weigh the mass.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid**
- b) **Hydrochloric acid (1+4, 1+10)**
- c) **Nitric acid (1+1)**
- d) **Hydrofluoric acid**
- e) **Sulfuric acid (1+1)**
- f) **Molybdenum (powder)** High purity molybdenum, which contains no silicon or the known content as low as possible.
- g) **Iron** High purity iron, which contains no silicon or the known content as low as possible.

3 Test portion Weigh out 1.0 g of the sample to the nearest 0.1 mg.

4 Operation

4.1 Decomposition and dehydration treatment of sample Decomposition and dehydration treatment of sample shall be in accordance with the following procedures.

- a) Weigh out a sample, transfer it to a beaker (300 ml) and cover it with a watch glass.
- b) Add 20 ml of nitric acid (1+1) and 5 ml of hydrochloric acid, and decompose the sample by gentle heating.
- c) After letting it cool, wash the bottom side of the watch glass with water and remove the watch glass.
- d) Add 20 ml of sulfuric acid (1+1), heat it and generate white fumes of sulfuric acid for about 15 minutes and let it cool.

4.2 Filtration and washing Filtration and washing shall be in accordance with the following procedure.

- a) Add 50 ml of hydrochloric acid (1+4) to the salts obtained in **4.1 d)**, heat (') and dissolve the soluble salts.
- b) Filter the solution immediately through a filter paper (Class 5B), remove the precipitates from the walls of beaker using a glass rod with rubber and transfer the precipitates onto the filter paper.

- c) Wash the filtrate with hydrochloric acid (1+10) warmed up 40 °C to 60 °C until iron (III) ion can not be detected in the filtrate. And then wash it with warm water until acid disappears. Discard the filtrate and washings.

Note (1) As hydrated silicon oxide get soluble again by heating for a long time, take care that dissolution of soluble salts is carried out in as short a time as possible, which is followed by immediate filtration.

4.3 Ashing and Weighing Ashing and weighing shall be in accordance with the following procedures.

- Transfer the precipitate with filter paper obtained in 4.2 c) to a platinum crucible (No. 30).
- After drying, incinerate the filter paper to ash at a low temperature.
- After igniting at least 1 100 °C for about 30 minutes, allow it to stand to room temperature in a desiccator.
- Repeat the operation c) until constant weight is reached.

4.4 Hydrofluoric acid treatment and weighing Hydrofluoric acid treatment and weighing shall be in accordance with the following procedures.

- Moisten the residue in the platinum crucible obtained in 4.3 d) by adding 2 to 3 drops of sulfuric acid (1+1), add 5 ml of hydrofluoric acid, heat it trying not to splash until white fumes of sulfuric acid are not generated, and evaporate silicon dioxide and sulfuric acid.
- Ignite the platinum crucible at least 1 100 °C for about 15 minutes and weigh the mass after allowing it to cool in desiccator.
- Repeat the operation b) until attaining to a constant weight.

5 Blank test Blank test is as follows : Weigh out 0.60 g of molybdenum [2 f)] and 0.40 g of iron [2 g)] in place of the sample, transfer them to the beaker (300 ml) and cover it with a watch glass. Hereafter, carry out the same operations of 4.1 b) to 4.4 c) as that of sample analysis, in parallel with the determination of the sample.

6 Calculation Calculate the content of silicon in a sample with the following formula.

$$Si = \frac{[(m_1 - m_2) - (m_3 - m_4)] \times 0.4674}{m} \times 100 + C$$

where Si : silicon contents in a sample [% (m/m)]

m_1 : mass of platinum crucible obtained in 4.3 d) for the sample (g)

m_2 : mass of platinum crucible obtained in 4.4 c) for the sample (g)

m_3 : mass of platinum crucible obtained in 4.3 d) in blank test (g)

m_4 : mass of platinum crucible obtained in 4.4 c) in blank test (g)

m : test portion (g)

C : weighted total of silicon content of molybdenum [2 f)] and iron [2 g)] used in blank test, by calculating the following formula [% (m/m)]

$$C = a \times 0.60 + b \times 0.40$$

where a : silicon content in molybdenum [2 f)] [% (m/m)]

b : silicon content in iron [2 g)] [% (m/m)]

Annex 6 (normative)**Determination of silicon — ICP emission spectrochemical method**

1 Summary Decompose the sample with sulfuric acid and nitric acid. Filter the solution, fuse the residue with sodium carbonate and dissolve the melt into the filtrate. Nebulize the solution into the argon plasma of an Inductively Coupled Plasma (ICP) emission spectrochemical analyser and measure the intensity of the emitted light from each element.

2 Reagents The reagents shall be as follows. Yttrium solution and silicon standard solution shall be stocked in a polyethylene bottle.

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid (1+1)**
- c) **Sulfuric acid (1+1)**
- d) **Sodium carbonate**
- e) **Molybdenum (powder)** High purity molybdenum, which contains no silicon or the known contents as low as possible.
- f) **Iron** High purity iron, which contains no silicon or the known contents as low as possible.
- g) **Yttrium solution (1 mg Y/ml)** Add 50 ml of hydrochloric acid (1+1) to 1.269 9 g of yttrium oxide (III) [purity at least 99.9 % (m/m)] and decompose by heating. After cooling it to the ordinary temperature, transfer the solution into a measuring flask (1 000 ml) and dilute to the marked line with water.
- h) **Silicon standard solution (0.10 mg Si/ml)** Weigh out 0.213 9 g of silicon dioxide [at least 99.95 % (m/m)] which was previously ignited for 1 hour at 1 000 °C and cooled down to the ordinary temperature in a desiccator. Transfer it into a platinum crucible (No. 30). Mix it with 1 g of sodium carbonate and fuse the mixture by heating. After allowing it to cool, dip the platinum crucible into a platinum dish (No. 150) or a polyethylene beaker (200 ml) containing 100 ml of warm water, and dissolve the melt thoroughly, wash the platinum crucible with water and take it out. After allowing it to cool to ordinary temperature, transfer the solution into a volumetric flask of 1 000 ml with water and dilute it to the marked line with water.

3 Test portion Weigh out 0.20 g of the sample to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of the sample Decomposition of the sample shall be in accordance with the following procedures.

- a) Weigh out the sample, transfer it to a beaker (300 ml) and cover it with a watch glass.
- b) After adding 5 ml of sulfuric acid (1+1), add 10 ml of nitric acid (1+1) a little by little and decompose it by heating.
- c) After cooling, wash the bottom side of the watch glass with water and remove the watch glass.

- d) Add 30 ml of water, filter the solution through filter paper (Class 5B) and remove the precipitates from the walls of beaker using a glass rod with rubber, and transfer the precipitate onto the filter paper.
- e) Wash the filtrate primarily with hydrochloric acid (1+50) warmed up to 40 °C to 60 °C until the iron (III) ion can not be detected in the filtrate. Wash with warm water until the acid disappears. Collect the filtrate and the washings to the beaker (200 ml).
- f) Concentrate the filtrate and the washings to be about 50 ml by heating.

4.2 Treatment of insoluble residue Treatment of the insoluble residue shall be carried out in accordance with the following procedures.

- a) Transfer the insoluble residue obtained in 4.1 e) and filter paper into a platinum crucible (No. 30) and incinerate the filter paper to ash by heating at a low temperature.
- b) After cooling, add 1.0 g of sodium carbonate, mix and cover.
- c) Heat while increasing temperature gradually and dissolve the residue thoroughly at about 900 °C.
- d) After letting it stand to cool, transfer the platinum crucible and its cover into the solution obtained in 4.1 f).
- e) Dissolve the melt with gentle heating and take out the platinum crucible and its cover by washing with water.
- f) After cooling the solution to room temperature, transfer it to a volumetric flask of 100 ml with water.

4.3 Preparation of the solution for measuring the emitted intensities Preparation of the solution for measuring the emitted intensities shall be in accordance with either one of the following methods.

- a) **For the application of the emitted intensities method** Dilute the solution obtained 4.2 f) to the marked line with water.
- b) **For the application of the intensities ratio method** After adding accurately 10 ml of yttrium solution [2 g] to the solution obtained in 4.2 f), dilute the volume to the marked line with water.

4.4 Measurements of the emitted intensities Measurements of emitted intensities shall be in accordance with either one of the following methods (¹).

- a) **For the application of the emitted intensities method** Nebulize a part of the solution obtained in 4.3 a) into an argon plasma of ICP emission spectrochemical analyzer and measure the emitted intensity of silicon at 288.16 nm in wavelength.
- b) **For the application of the intensities ratio method** Nebulize a part of the solution obtained in 4.3 b) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of silicon at 288.16 nm in wavelength and that of yttrium at 371.03 nm in wavelength. Calculate the ratio of silicon intensity to yttrium intensity.

Note (¹) Fundamental operation of measurement shall be in accordance with 5 in JIS

K 0116.

5 Blank test The emitted intensity or intensity ratio of the solution to which silicon standard solution is not added is obtained in the preparation of the working curve of **6** and used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.12 g of molybdenum [**2 e**] and 0.08 g of iron [**2 f**], transfer them into several beakers (300 ml) and cover with the watch glasses.
- b) Carry out the same operation as in the sample in accordance with the procedures of **4.1 b**) to **4.2 f**).
- c) Add stepwise accurate volume of 0 ml to 20 ml of standard silicon solution gradually (it corresponds to 0 mg to 2.0 mg of silicon) in each beaker.
- d) Carry out the same operation as in the sample in accordance with the procedures of **4.3** and **4.4**.
- e) Prepare the correlation curve between the emitted intensity or intensity ratio obtained and total amounts of silicon content added as the silicon standard solution in **c**) and silicon content in molybdenum and iron added in **a**). Use this correlation curve as working curve.

7 Calculation Silicon content in sample shall be calculated in accordance with following formula.

$$Si = \frac{A - B}{m} \times 100 + C$$

where Si : silicon content in the sample [% (m/m)]

A : detected amount of silicon in sample solution (g)

B : detected amount of silicon in blank test solution (g)

m : test portion (g)

C : weighted total of silicon content [% (m/m)] in molybdenum [**2 e**] and iron [**2 f**] used in blank test, which shall be calculated in accordance with the following formula.

$$C = a \times 0.12 + b \times 0.08$$

where a : silicon content in molybdenum [**2 e**] [% (m/m)]

b : silicon content in iron [**2 f**] [% (m/m)]

Annex 7 (normative)**Determination of phosphorous — Beryllium hydroxide coprecipitation separation phosphomolybdic acid blue absorptiometric method**

1 Summary Decompose a sample with nitric acid and hydrofluoric acid, add sulfuric acid, heat and generate white fumes of sulfuric acid, dissolve the salts with hydrochloric acid, add beryllium sulfate, coprecipitate phosphorous with beryllium hydroxide by liquid ammonia and filter it. Dissolve the precipitate with nitric acid, add perchloric acid, heat and generate white fumes of perchloric acid, reduce iron with adding sodium hydrogen sulfite and generate phosphomolybdic acid blue with adding hexaammonium heptamolybdate and hydrazinium sulfate. Measure its absorbance with spectrophotometer.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid (1+1, 1+2, 1+50)**
- b) **Nitric acid(1+1, 1+2, 1+50)**
- c) **Perchloric acid**
- d) **Hydrofluoric acid**
- e) **Sulfuric acid (1+1)**
- f) **Hydrobromic acid**
- g) **Ammonia water**
- h) **Molybdenum (powder)** High purity molybdenum, which contains no phosphorous or the known content as low as possible.
- i) **Iron** High purity iron, which contains no phosphorous or the known content as low as possible.
- j) **Disodium dihydrogen ethylenediaminetetraacetate dihydrate** (Hereafter referred to as EDTA2Na.)
- k) **Beryllium sulfate solution** Dissolve 19.7g of beryllium sulfate tetrahydrate to 20 ml of sulfuric acid (1+3) and dilute the volume to 1 000 ml with water.

WARNING FOR SAFETY As beryllium sulfate is heavily poisonous, the reagent, its solution and the solution containing these shall be handled carefully.

- l) **Sodium hydrogen sulfite (100 g/l)**
- m) **Color producing reagent solution** Prepare the following 2 types of solutions, previously. Mix 25 ml of A solution, 10 ml of B solution and 65 ml of water before use.

A solution : Dissolve 20 g of hexaammonium heptamolybdate tetrahydrate in 100 ml of warm water, add 700 ml of sulfuric acid (1+1), cool it to room temperature and dilute the volume to 1 000 ml with water.

B solution : Hydrazinium sulfate solution (1.5 g/l)

- n) **Phosphorous standard solution (0.10 mg P/ml)** Weigh out 0.439 4 g of potassium dihydrogen phosphate which has been dried at 110 °C to constant weight, cooled in a desiccator and stocked. Dissolve it with water, transfer the solution to a volumetric flask

of 1 000 ml with water and dilute to the marked line with water.

3 Test portion Weigh out 0.50 g of the sample to the nearest 0.1 mg.

4 Operation

WARNING FOR SAFETY Perchloric acid fumes may produce explosions in the presence of ammonia, nitrous acid vapor or organic substances in general. The vapor should be treated out in well ventilated area installed with a local exhaust ventilator to be safe when perchloric acid is used.

4.1 Decomposition of sample Decomposition of sample shall be in accordance with the following procedures.

- a) Weigh out the sample, transfer it to a platinum dish (No. 100) and cover with a lid.
- b) Add 10 ml of nitric acid (1+1), add dropwise hydrofluoric acid and, decompose the sample with cooling by water in case of violent reaction.
- c) After finishing of violent reaction, add further 5 ml of hydrofluoric acid and remove the lid after washing the bottom of the lid with water.
- d) Add 10 ml of sulfuric acid (1+1) and continue to heat until white fumes of sulfuric acid are not generated.
- e) After cooling, add 35 ml of hydrochloric acid (1+2) and heat to dissolve the soluble salts.
- f) Dilute the solution with warm water to about 50 ml, filter the solution through filter paper (Class 5B) and wash with hydrochloric acid (1+50) warmed up to 40 °C to 60 °C until iron (III) ion can not be detected in the filtrate. Wash it with warm water for 3 to 4 times, collect the filtrate and the washings to a beaker (300 ml) and dilute the volume to 100 ml with water.

4.2 Separation of phosphorous Separation of phosphorous shall be carried out in accordance with the following procedures.

- a) Add 4.0 g of EDTA2Na to the solution obtained in 4.1 f) and heat moderately to decompose it covering with a watch glass.
- b) After cooling, add 5 ml of beryllium sulfate solution [2 k)], add ammonia water to maintain pH 10 measured with a pH meter and precipitate beryllium hydroxide.
- c) After heating to boil for 2 minutes, cool down to room temperature, wash the bottom side of the watch glass and remove it.
- d) Filter the precipitate through filter paper (Class 5B) and wash 4 to 5 times with warm water.
- e) Wash off the precipitate into the said beaker by spraying water, place this beaker under the funnel, dissolve the precipitate attached to the filter paper by pouring little by little 20 ml of nitric acid (1+2) warmed at 40 °C to 60 °C..
- f) Wash the filter paper with nitric acid (1+50) warmed up to 40 °C to 60 °C.

- g) Add 10 ml of perchloric acid to this solution, cover with a watch glass and continue to heat for about 10 minutes in a state where the vapor of perchloric acid flows backward along the inside wall of beaker (¹).
- h) After cooling, add about 50 ml of warm water, dissolve the soluble salts by heating and remove the watch glass after washing the bottom side of watch glass.
- i) Filter the solution through filter paper (Class 5A), wash sufficiently with warm water, combine the filtrate and the washings.
- j) After cooling down to the ordinary temperature, transfer the solution to a volumetric flask of 250 ml with water and dilute to the marked line with water.

Note (¹) When at least 0.5 mg of arsenic coexists in the solution, after allowing it to cool, add 5 ml of hydrochloric acid (1+1) and 5 ml of hydrobromic acid, generate again white fumes of perchloric acid and follow the procedure h).

4.3 Coloration Coloration shall be carried out in accordance with the following procedures.

- a) Take separately 25 ml of the solution obtained in 4.2 j) and transfer it into a volumetric flask of 100 ml.
- b) Add 10 ml of sodium hydrogen sulfite solution, heat it in the boiled water bath until the solution becomes colorless, add immediately 25 ml of coloration reagent solution [2 m)] and heat it again in the boiled water bath for about 15 minutes.
- c) Cool the solution to the ordinary temperature in running water and dilute it up to the marked line with water.

4.4 Measurement of absorbance Transfer a portion of colored solution obtained in 4.3 c) into the absorption cell (10 mm) of spectrophotometer and measure the absorbance at near 825 nm in wavelength.

5 Blank test Weigh out 0.30 g of molybdenum [2 h)] and 0.20 g of iron [2 i)] in place of sample, transfer it to a platinum dish (No. 100) and cover with a lid. Hereafter, carry out the same operation of the sample according to the procedures in 4.1 b) to 4.4 in parallel with the determination of phosphorous in the sample.

6 Preparation of working curve Working curve shall be prepared according to the following procedure.

- a) Add correctly stepwise 0 ml to 5.0 ml of phosphorous standard solution [2 n)] (which corresponds to 0 mg to 0.5 mg as phosphorous) to several beakers (100 ml) separately.
- b) Add 5 ml of perchloric acid respectively and generate white fumes of perchloric acid by heating.
- c) After cooling, dissolve the soluble salts by adding 30 ml of warm water.
- d) Transfer it into a volumetric flask of 250 ml with water and cool to ordinary temperature and dilute it up to the marked line with water.
- e) Hereafter, carry out the same operation as that of sample analysis according to the

procedures of 4.3 and 4.4.

- f) Prepare the correlation curve by plotting the obtained absorbance against the amount of phosphorous added as phosphorous standard solution and parallel transfer the correlation curve so as to pass through the origin and take it as a working curve.

7 Calculation Phosphorous content in sample shall be calculated by the following formula.

$$P = \frac{A - B}{m \times \frac{1}{10}} \times 100 + C$$

where P : phosphorus content in the sample [% (m/m)]

A : detected amount of phosphorus in aliquot sample solution (g)

B : detected amount of phosphorus in aliquot blank test solution (g)

m : test portion (g)

C : weighted total of phosphorous content [% (m/m)] in molybdenum [2 h)] and iron [2 i)] used in blank test, which shall be calculated in accordance with the following formula.

$$C = a \times 0.30 + b \times 0.20$$

where a : phosphorous content in molybdenum [2 h)] [% (m/m)]

b : phosphorous content in iron [2 i)] [% (m/m)]

Annex 8 (normative)**Determination of phosphorous — Beryllium hydroxide coprecipitation
separation ICP emission spectrochemical method**

1 Summary Decompose a sample with nitric acid and hydrofluoric acid, add sulfuric acid, heat and generate white fumes of sulfuric acid. Dissolve it with hydrofluoric acid, add beryllium sulfate, add ammonia water, coprecipitate phosphorous with beryllium hydroxide and filter it. Dissolve the precipitate with nitric acid. Nebulize the solution into an argon plasma of the Inductively Coupled Plasma (ICP) emission spectrochemical analyzer and measure the emitted intensity by each element.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid (1+1)**
- c) **Perchloric acid**
- d) **Hydrofluoric acid**
- e) **Sulfuric acid (1+1)**
- f) **Ammonia water**
- g) **Molybdenum (powder)** High purity molybdenum, which contains no phosphorous or the known content as low as possible.
- h) **Iron** High purity iron, which contains no phosphorous or the known content as low as possible.
- i) **Disodium dihydrogen ethylenediamine tetraacetate dihydrate** (hereafter referred to as EDTA2Na)
- j) **Beryllium sulfate solution** Dissolve 19.7 g of beryllium sulfate tetrahydrate to 20 ml of sulfuric acid (1+3) and dilute the volume with water to 1 000 ml.

WARNING FOR SAFETY As beryllium sulfate is a deadly poison, the reagent, its solution and the solution containing these shall be handled carefully.

- k) **Yttrium solution (1 mg Y/ml)** Add 50 ml of hydrochloric acid (1+1) to 1.269 9 g of yttrium oxide (III) [at least 99.9 % (m/m)] and decompose by heating. After cooling it to ordinary temperature, transfer the solution into a volumetric flask of 1 000 ml with water and dilute to the marked line with water.
- l) **Phosphorous standard solution (0.10 mg P/ml)** Weigh out 0.439 4 g of potassium dihydrogen phosphate which has been dried at 110 °C to constant weight, cooled down in desiccator and stocked. Dissolve it with water, transfer the solution to a volumetric flask of 1 000 ml with water and dilute to the marked line with water.

3 Test portion Weigh out 1.0 g of a sample to the nearest 0.1 mg.

4 Operation

WARNING FOR SAFETY Perchloric acid fumes may produce explosions in the

presence of ammonia, nitrous acid vapor or organic substances in general. The vapor should be treated out in well ventilated area installed with a local exhaust ventilator to be safe when perchloric acid is used.

4.1 Decomposition of sample Decomposition of sample shall be carried out in accordance with the following procedures.

- a) Weigh out the sample, transfer to a platinum dish (No. 100) and cover with a lid.
- b) Add 20 ml of nitric acid (1+1), add dropwise hydrofluoric acid and decompose the sample with cooling by water in case of violent reaction.
- c) After finishing of violent reaction, add further 5 ml of hydrofluoric acid.
- d) Remove the lid after washing the bottom of the lid with water.
- e) Add 10 ml of sulfuric acid (1+1) and heat to evaporate until white fumes of sulfuric acid are not generated.
- f) After cooling, add 35 ml of hydrochloric acid (1+2) and heat to dissolve the soluble salts.
- g) Dilute the solution with warm water to about 50 ml volume, filter the solution through filter paper (Class 5B) and wash with hydrochloric acid (1+50) warmed up to 40 °C to 60 °C until iron (III) ion can not be detected in the filtrate. Wash it 3 to 4 times with warm water, collect the filtrate and the washings to a beaker (300 ml) and dilute the volume to 100 ml with water.

4.2 Separation of phosphorous Separation of phosphorous shall be carried out in accordance with the following procedures.

- a) Add 4.0 g of EDTA2Na to the solution obtained in 4.1 g) and heat moderately to decompose it covering with a watch glass.
- b) After cooling, add 5 ml of beryllium sulfate solution [2 j)], add ammonia water to maintain pH 10 measured with a pH meter and precipitate beryllium hydroxide.
- c) After heating to boil for 2 minutes, cool down to room temperature, wash the bottom side of the watch glass and remove it.
- d) Filter the precipitate through filter paper (Class 5B) and wash 4 to 5 times with warm water.
- e) Wash off the precipitate into the said beaker by spraying water, place this beaker under the funnel, dissolve the precipitate attached to the filter paper by pouring little by little 20 ml of nitric acid (1+2) warmed at 40 °C to 60 °C.
- f) Wash the filter paper with nitric acid (1+50) warmed up to 40 °C to 60 °C.
- g) Add 10 ml of perchloric acid to this solution, cover with a watch glass
- h) Continue to heat for about 10 minutes in a state where the vapor of perchloric acid flows backward along the inside wall of beaker (').
- i) After cooling, add 50 ml of warm water, dissolve the soluble salts by heating and remove the watch glass after washing the bottom side of watch glass.

- j) Filter the solution through filter paper (Class 5A), wash sufficiently with warm water and combine the filtrate and the washings.
- k) After cooling down to the ordinary temperature, transfer the solution to a volumetric flask of 100 ml with water and dilute to the marked line with water.

Note (1) When at least 0.5 mg of arsenic coexists in the solution, after allowing it to cool, add 5 ml of hydrochloric acid (1+1) and 5 ml of hydrobromic acid, generate again white fumes of perchloric acid and follow the procedure i).

4.3 Preparation of the solution for measuring the emitted intensities Preparation of the solution for measuring the emitted intensities shall be in accordance with either one of the following methods.

- a) **For the application of the emitted intensities method** Dilute the solution obtained in 4.2 h) to the marked line with water.
- b) **For the application of the intensities ratio method** After adding accurately 10 ml of yttrium solution [2 k)] to the solution obtained in 4.2 h), dilute up to the marked line with water.

4.4 Measurements of the emitted intensities Measurements of emitted intensities shall be in accordance with either one of the following methods (2).

- (a) **For the application of the emitted intensities method** Nebulize a part of the solution obtained in 4.3 a) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of phosphorous at 213.62 nm in wavelength.
- (b) **For the application of the intensities ratio method** Nebulize a part of the solution obtained in 4.3 b) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of phosphorous at 213.62 nm in wavelength and yttrium at 371.03 nm in wavelength. Calculate the ratio of phosphorous intensity to yttrium intensity.

Note (2) Fundamental operation of measurement shall be in accordance with 5 in JIS K 0116.

5 Blank test The emitted intensity or intensity ratio of the solution to which standard phosphorous solution is not added is obtained in the preparation of the working curve of 6 and used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.60 g of molybdenum [2 g)] and 0.40 g of iron [2 h)], transfer them into several platinum dishes (No.100) and cover with lids.
- b) Carry out in accordance with the procedures of 4.1 b) to 4.2 k), add stepwise accurate volume of 0 ml to 20 ml of phosphorous standard solution [2 l)] gradually (which corresponds to 0 mg to 1.0 mg of phosphorous).
- c) Carry out in accordance with the procedures of 4.3 and 4.4.
- d) Prepare the correlation curve between the emitted intensity or intensity ratio obtained

and total amounts of content added as the phosphorous standard solution and phosphorous content in molybdenum and iron. Use this correlation curve as working curve

7 Calculation Phosphorous content in sample shall be calculated in accordance with following formula.

$$P = \frac{A-B}{m} \times 100 + C$$

where P : phosphorus content in the sample [% (m/m)]

A : detected amount of phosphorus in sample solution (g)

B : detected amount of phosphorus in blank test solution (g)

m : test portion (g)

C : weighted total of phosphorous content [% (m/m)] in molybdenum [2 g] and iron [2 h] used in the blank test, which shall be calculated in accordance with the following formula.

$$C = a \times 0.60 + b \times 0.40$$

where a : phosphorous content in molybdenum [2 g] [% (m/m)]

b : phosphorous content in iron [2 h] [% (m/m)]

Annex 9 (normative)**Determination of sulfur — Combustion-potassium iodic acid titrimetric method**

1 Summary Heat a sample at a high temperature in an oxygen gas current, oxidize sulfur to sulfur dioxide, etc., let it be absorbed by hydrochloric acid absorption solution and titrate it with potassium iodic acid standard solution as an indicator of starch solution containing potassium iodine.

2 Reagents The reagents shall be in accordance with 7.3 (2) of JIS Z 2616.

3 Apparatus The apparatus shall be in accordance with 5 of JIS Z 2616.

4 Equipment and materials The equipment and materials shall be in accordance with 6 in JIS Z 2616.

5 Test portion Weigh out 1.0 g of the sample to the nearest 0.1 mg. When a high frequency induction heating furnace is used, 0.50 g may be weighed out.

6 Operation

WARNING FOR SAFETY In the combustion process, it shall be taken care that tongs for a crucible shall always be used in handling of a combustion boat heated at a high temperature or a combustion crucible for fear that the skin or fingers of an operator may be burned. And efforts shall be made to prevent occurrence of a fire by paying attention to the treatment of excessive exhaust oxygen gas.

6.1 Preparation for operation The preparation for operation shall be in accordance with 7.3 (4) in JIS Z 2616.

When a tubular electric resistance heating furnace is used, the temperature in the combustion tube shall be kept at 1 400 °C to 1 450 °C ⁽¹⁾.

When a high frequency induction heating furnace is used, the conditions for high frequency induction heating shall be set up ⁽²⁾.

Notes⁽¹⁾ Adjust the temperature paying regard to the differences between the temperature inside of combustion tube and that of thermometer indication.

⁽²⁾ For example, the parameter, such as anodic current of high frequency oscillator and grid current which are depending on the specification of the applied equipment.

6.2 Determination The determination shall be carried out in accordance with 7.3 (5) in JIS Z 2616 ⁽³⁾.

A high frequency induction heating furnace may be used. However, in this case, the crucible shall be used and the oxygen gas shall flow with the rate of 1 500 ml per min.

Note ⁽³⁾ Add an accelerator 1 to 5 times as much as the sample, which shall be selected from the accelerators listed on 6.12 in JIS Z 2616, if necessary. The

most suitable kind and optimum mass of accelerator shall be selected for the apparatus used.

7 Blank test The blank test shall be carried out in accordance with 7.3 (6) in JIS Z 2616.

When an accelerator by which induction current is not generated in a high frequency induction heating furnace is used, add 0.5 g to 1.0 g of iron in which sulfur content is as low as possible and known and carry out the procedure. Subtract the amount of sulfur contained in the added iron from that in the blank test.

8 Calculation Calculate the content of sulfur in a sample according to 7.3 (7) in JIS Z 2616.

Annex 10 (normative)
Determination of sulfur — Combustion-infrared absorption method

1 Summary Heat a sample in an oxygen gas current at a high temperature, oxidize sulfur to sulfur dioxide, send this together with oxygen to an infrared absorption detector, and measure the infrared absorption of sulfur dioxide.

2 Apparatus The apparatus shall be in accordance with 7.7 (2) or 7.8 (2) in JIS Z 2616.

3 Equipment and materials The equipment and materials shall be in accordance with 6 in JIS Z 2616.

4 Test portion Test portion shall be the optimum mass for the apparatus used.

Remarks : Test portion is 0.5 g to 1.0 g in general.

5 Operation

WARNING FOR SAFETY In the combustion process, it shall be taken care that a pair of tongs for a crucible shall always be used in handling of a combustion boat heated at a high temperature or a combustion crucible for fear that the skin or fingers of an operator may be burned.

And efforts shall be made to prevent occurrence of a fire by paying attention to the treatment of excessive exhaust oxygen gas.

5.1 Preparation for operation The preparation for operation shall be in accordance with 7.7 (3) or 7.8 (3) in JIS Z 2616. In the calculation of sulfur content per indication value, the reference material for iron and steel may be used.

5.2 Determination The determination shall be in accordance with 7.7 (4) or 7.8 (4) of JIS Z 2616 (1).

Note (1) Add an accelerator. Select the most suitable kind of the accelerator from those listed in 6.12 in JIS Z 2616. Add an accelerator 2 to 4 times the amount of the sample and mix thoroughly or cover it over the sample.

6 Blank test Blank test shall be carried out in accordance with 7.7 (5) or 7.8 (5) in JIS Z 2616.

7 Calculation Calculation shall be in accordance with 7.7 (6) or 7.8 (6) in JIS Z 2616.

Annex 11 (normative)**Determination of copper — Atomic absorption spectrophotometric method**

1 Summary Decompose a sample with sulfuric acid and nitric acid and heat to generate white fumes of sulfuric acid. Dissolve the salts with hydrochloric acid, spray into the flame of air-acetylene of atomic absorption spectrophotometer and measure the absorbance.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid (1+1)**
- c) **Sulfuric acid (1+1)**
- d) **Molybdenum (powder)** High purity molybdenum, which contains no copper or the known content as low as possible.
- e) **Iron** High purity iron, which contains no copper or the known content as low as possible.
- f) **Copper standard solution (0.50 mg Cu/ml)** Weigh out 0.500 g of copper [at least 99.9 % (m/m)], transfer it into a beaker (300 ml), cover with a watch glass, add 10 ml of sulfuric acid (1+1) and 20 ml of nitric acid (1+1) and decompose by gentle heating. After cooling, wash the bottom surface of watch glass with water and remove it. Heat to generate white fumes of sulfuric acid. After cooling, wash the inner wall of beaker with a small amount of water, heat again to generate white fumes of sulfuric acid and cool. Add about 50 ml of water to dissolve soluble salts, transfer it into a volumetric flask of 1 000 ml with water and dilute up to the marked line with water.

3 Test portion Weigh out 0.50 g of sample to the nearest 0.1 mg.

4 Operation

4.1 Preparation of sample solution Preparation of sample solution shall be carried out according to the following procedures.

- a) Weigh out a sample, transfer it into a beaker (200 ml) and cover it with a watch glass.
- b) Add 10 ml of sulfuric acid (1+1) and 20 ml of nitric acid (1+1) and heat to decompose.
- c) Wash the bottom surface of the watch glass with water, remove it and continue to heat until the generation of the white fumes of sulfuric acid is nearly finished.
- d) After cooling, add 20 ml of hydrochloric acid (1+1) and heat to dissolve soluble salts.
- e) Filter the solution through filter paper (Class 5A) and wash it sufficiently with hydrochloric acid (1+50) warmed up to 40 °C to 60 °C.
- f) Transfer the filtrate and the washings into a volumetric flask of 100 ml with water. After cooling to ordinary temperature, dilute it up to the marked line with water.

4.2 Measurement of absorbance Spray a part of the solution obtained in 4.1 f) into the flame of air-acetylene of atomic absorption spectrophotometer after having adjusted zero

reading with water nebulizing, and measure the absorbance of copper at 324.7 nm in wavelength.

5 Blank test In preparation of working curve in 6, the absorbance, measured in the solution in which copper standard solution is not added, is used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be carried out in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.30 g of molybdenum [2 d)] and 0.20 g of iron [2 e)], transfer them into several beakers (300 ml) and cover with the watch glasses.
- b) Carry out the same operation as in the sample in accordance with the procedure of 4.1 b) to f).
- c) Add accurately stepwise 0 ml to 5.0 ml of standard copper solution gradually (which corresponds to 0 mg to 25 mg of copper). Dilute to the marked line with water.
- d) Hereafter, carry out the same operation as in the sample in accordance with the procedure of 4.2.
- e) Prepare the correlation curve by plotting the obtained absorbance against the amount of copper added as copper standard solution and displace the curve parallel so as to pass through the origin of the figure to make the working curve.

7 Calculation Copper content in sample shall be calculated in accordance with following formula.

$$Cu = \frac{A-B}{m} \times 100 + C$$

where Cu : copper content in the sample [% (m/m)]

A : detected amount of copper in sample solution (g)

B : detected amount of copper in blank test solution (g)

m : test portion (g)

C : weighted total of copper content in molybdenum [2 d)] and iron [2 e)] used in blank test, which shall be calculated in accordance with the following formula.

$$C = a \times 0.30 + b \times 0.20$$

where a : copper content in molybdenum [2 d)] [% (m/m)]

b : copper content in iron [2 e)] [% (m/m)]

Annex 12 (normative)**Determination of copper — ICP emission spectrochemical method**

1 Summary Decompose a sample with sulfuric acid and nitric acid and heat to generate white fumes of sulfuric acid. Dissolve with hydrochloric acid and filter it and dissolve the insoluble residue with potassium disulfate into the solution. Nebulize the solution into an argon plasma of an ICP emission spectrochemical analyzer and measure the intensity of the emitted light.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid (1+1)**
- c) **Hydrofluoric acid**
- d) **Sulfuric acid (1+1)**
- e) **Potassium disulfate**
- f) **Molybdenum (powder)** High purity molybdenum, which contains no copper or the known content as low as possible.
- g) **Iron** High purity iron, which contains no copper or the known content as low as possible.
- h) **Yttrium solution (1 mg Y/ml)** Add 50 ml of hydrochloric acid (1+1) to yttrium oxide (III) [purity at least 99.9 % (m/m)] and decompose by heating. After cooling it to the ordinary temperature, transfer the solution into a volumetric flask of 1 000 ml and dilute to the marked line with water.
- i) **Copper standard solution (1.0 mg Cu/ml)** Weigh out 1.000 g of copper [at least 99.9 % (m/m)], transfer it into a beaker (300 ml), cover with a watch glass, add 10 ml of sulfuric acid (1+1) and 20 ml of nitric acid (1+1) and decompose by gentle heating. After cooling, wash the bottom surface of watch glass with water and remove it. Heat to generate white fumes of sulfuric acid. After cooling, wash the inner wall of beaker with a small amount of water, heat again to generate white fumes of sulfuric acid and thereafter cool. Add about 50 ml of water to dissolve the soluble salts, transfer it into a volumetric flask of 1 000 ml and dilute up to the marked line with water.

3 Test portion Weigh out 1.0 g of sample to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of sample The decomposition of the sample shall be carried out in accordance with the following procedures.

- a) Weigh out a sample, transfer it into a polytetrafluoroethylene (hereafter refer to PTFE) beaker (200 ml) or a platinum dish (No. 100) and cover with a lid.
- b) Add 10 ml of sulfuric acid (1+1) and then add 20 ml of nitric acid (1+1) little by little. Decompose by heating and cool it. Wash the bottom side of the lid with water and remove it.

- c) Add 5 ml of hydrofluoric acid and heat to generate white fumes of sulfuric acid for about 15 minutes.
- d) After cooling, add 30 ml of water and 5 ml of hydrochloric acid and heat to dissolve the soluble salts.
- e) Filter the solution through filter paper (Class 5B) and remove the precipitates from the wall of beaker using a glass rod with rubber and transfer it onto the filter paper.
- f) Wash the filtrate by initially hydrochloric acid (1+50) warmed up to 40 °C to 60 °C until the iron (III) ion can not be detected in the filtrate. Wash it with warm water until acid disappears.
- g) Collect the filtrate and the washings to a beaker (200 ml) and heat to concentrate the filtrate and the washings to about 50 ml.

4.2 Treatment of insoluble residue Treatment of insoluble residue shall be carried out in accordance with the following procedures (¹).

- a) Transfer the insoluble residue obtained in 4.1 f) and the filter paper into a platinum crucible (No. 30) and incinerate the filter paper to ash by heating at a low temperature.
- b) After cooling, moisten the residue in the platinum crucible with 2 or 3 drops of sulfuric acid (1+1) add about 5 ml of hydrofluoric acid and heat to vaporize silicon dioxide and sulfuric acid, taking care not to splash it.
- c) After cooling, add 1.0 g of potassium disulfate and cover with a lid. Increase the temperature gradually, heat the crucible at about 700 °C and fuse the residue perfectly.
- d) After cooling, put the platinum crucible and the lid into the solution obtained in 4.1 g) and heat gently to dissolve the melt. Wash the platinum crucible and the lid with water and remove it.
- e) After cooling the solution to ordinary temperature, transfer it to a volumetric flask of 100 ml with water.

Note (¹) When insoluble residue is absent, the operation 4.2 may be eliminated. In this case, operate the solution obtained in 4.1 g) in accordance with the procedure of 4.2 e). Solution for working curve shall be operated under the same procedure.

4.3 Preparation of the solution for measuring the emitted intensities Preparation of the solution for measuring the emitted intensities shall be in accordance with either one of the following methods.

- (a) **For the application of the emitted intensities method** Dilute the solution obtained 4.2 e) to the marked line with water.
- (b) **For the application of the intensities ratio method** After adding accurately 10 ml of yttrium solution [2 h)] to the solution obtained in 4.2 e), dilute the volume to the marked line with water.

4.4 Measurements of the emitted intensities Measurements of emitted intensities shall be in accordance with either one of the following methods (²).

- a) **For the application of the emitted intensities method** Nebulize a part of the solution obtained in 4.3 a) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of copper at 327.40 nm in wavelength.
- b) **For the application of the intensities ratio method** Nebulize a part of the solution obtained in 4.3 b) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of copper at 327.40 nm in wavelength and that of yttrium at 371.03 nm in wavelength. Calculate the ratio of copper intensity to yttrium intensity.

Note (2) Fundamental operation of measurement shall be in accordance with 5 in JIS K 0116.

5 Blank test The emitted intensity or intensity ratio measured in the solution to which copper standard solution is not added in 6 the preparation of the working curve, is used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.60 g of molybdenum [2 f)] and 0.40 g of iron [2 g)], transfer them into several numbers of PTFE beakers (200 ml) or platinum dishes (No. 100) and cover with lids.
- b) Carry out the same operation as in the sample in accordance with the procedures of 4.1 b) to 4.2 e). Add correctly stepwise 0 ml to 5 ml of standard copper solution gradually (which corresponds to 0 mg to 5 mg of copper) into each beaker.
- c) Carry out the same operation as in the sample in accordance with the procedure of 4.3 and 4.4.
- d) Prepare the correlation curve between the intensity or intensity ratio obtained and total amounts of copper content added as the copper standard solution and copper content in molybdenum and iron. Use this correlation curve as working curve.

7 Calculation Copper content in sample shall be calculated in accordance with the following formula.

$$Cu = \frac{A-B}{m} \times 100 + C$$

where Cu : copper content in the sample [% (m/m)]

A : detected amount of copper in sample solution (g)

B : detected amount of copper in blank test solution (g)

m : test portion (g)

C : weighted total of copper content in molybdenum [2 f)] and iron [2 g)] used in blank test, which shall be calculated in accordance with the following formula.

$$C = a \times 0.60 + b \times 0.40$$

where a : copper content in molybdenum [2 f)] [% (m/m)]

b : copper content in iron [2 g] [% (m/m)]

Annex 13 (normative)**Determination of aluminum — Atomic absorption spectrophotometric method**

1 Summary Decompose a sample with hydrochloric acid, nitric acid and sulfuric acid, heat to generate the white fumes of sulfuric acid, concentrate, dry up, dissolve the salts with hydrochloric acid and filter it. Fuse the insoluble residue with potassium disulfate and dissolve it into the filtrate and the washings. Nebulize the solution into the flame of dinitrogen oxide-acetylene in the atomic absorption spectrophotometer and measure its absorbance.

2 Reagents The reagents shall be as follows :

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid**
- c) **Hydrofluoric acid**
- d) **Sulfuric acid (1+1)**
- e) **Molybdenum (powder)** High purity molybdenum, which contains no aluminum or the known content as low as possible.
- f) **Iron** High purity iron, which contains no aluminum or the known content as low as possible.
- g) **Potassium disulfate**
- h) **Aluminum standard solution (0.10 mg Al/ml)** Weigh out 0.100 g of aluminum [at least 99.95 % (m/m)], transfer it into an Erlenmeyer flask (300 ml), put a funnel into an opening of the flask, add 5 ml of hydrochloric acid (1+1) and heat it gently to decompose. After cooling to ordinary temperature, transfer the solution into a volumetric flask of 1 000 ml with water and dilute up to the marked line with water.

3 Test portion Weigh out 0.50 g of sample to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of sample The decomposition of sample shall be carried out in accordance with the following procedures.

- a) Weigh out a sample, transfer it into a beaker (200 ml) and cover with a watch glass.
- b) Add 20 ml of hydrochloric acid (1+1) and 5 ml of nitric acid, heat gently to dissolve and cool it. Wash the bottom surface of watch glass and remove it.
- c) Add 10 ml of sulfuric acid (1+1) and heat the solution until white fumes of sulfuric acid are hardly generated.
- d) After cooling, add 20 ml of hydrochloric acid (1+1), heat to dissolve the soluble salts and dilute the volume up to about 50 ml with warm water.
- e) Filter the solution through filter paper (Class 5B), remove the insoluble residue from the inside wall of beaker using a glass rod with rubber and transfer it onto the filter paper.
- f) Initially, wash the filtrate with hydrochloric acid (1+50) warmed at 40 °C to 60 °C until

the iron (III) ion can not be detected in the filtrate. Then, wash it with warm water until acid disappears.

- g) Collect the filtrate and the washings to the beaker (200 ml) and heat to concentrate the filtrate and washings to about 50 ml.

4.2 Treatment of insoluble residue Treatment of insoluble residue shall be carried out in accordance with the following procedures.

- a) Transfer the insoluble residue obtained in 4.1 f) and filter paper into a platinum crucible (No. 30) and incinerate the filter paper to ash by heating at a low temperature.
- b) After cooling, moisten the residue in the platinum crucible with 2 or 3 drops of sulfuric acid (1+1), add 5 ml of hydrofluoric acid and heat to vaporize silicon dioxide and sulfuric acid, taking care not to splash it.
- c) After cooling, add 1.0 g of potassium disulfate and cover with a lid. Raise the temperature gradually, heat the crucible at about 700 °C and melt the residue thoroughly.
- d) After cooling, put the platinum crucible and the lid into the solution obtained in 4.1 g) and heat gently to dissolve the melt. Wash the platinum crucible and the lid with water and remove it.
- e) After cooling down to ordinary temperature, transfer it to a volumetric flask of 100 ml with water and dilute it with water.

4.3 Measurement of absorbance Nebulize a part of the solution obtained in 4.2 e) into the flame of dinitrogen oxide-acetylene in atomic absorption spectrophotometer after having adjusted zero reading with water nebulizing. Measure absorbance of aluminum at 309.3 nm or 396.2 nm in wavelength.

5 Blank test The absorbance measured in the solution to which aluminum standard solution is not added in 6 the preparation of the working curve, is used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be carried out in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.30 g of molybdenum [2 e)] and 0.20 g of iron [2 f)], transfer them into several beakers (200 ml) and cover with watch glasses.
- b) Carry out the same operation as in the sample in accordance with the procedures of 4.1 b) to 4.2 d).
- c) Transfer the solution to a volumetric flask of 100 ml, add correctly stepwise 0 ml to 10 ml of aluminum standard solution [2 h)] gradually (it corresponds to 0 mg to 1.0 mg of aluminum) and dilute it up to the marked line with water.
- d) Hereafter, carry out the same operation as in the sample in accordance with the procedure of 4.3.
- (e) Prepare the correlation curve by plotting the obtained absorbance against the amount of aluminum added as aluminum standard solution and displace the curve parallel so as to pass through the origin of the figure to make the working curve.

7 Calculation Aluminum content in sample shall be calculated in accordance with the following formula.

$$Al = \frac{A-B}{m} \times 100 + C$$

where Al : aluminum content in the sample [% (m/m)]

A : detected amount of aluminum in sample solution (g)

B : detected amount of aluminum in blank test solution (g)

m : test portion (g)

C : weighted total of aluminum content in molybdenum [2 e)] and iron [2 f)] used in blank test, which shall be calculated in accordance with the following formula

$$C = a \times 0.30 + b \times 0.20$$

where a : aluminum content in molybdenum [2 e)] [% (m/m)]

b : aluminum content in iron [2 f)] [% (m/m)]

Annex 14 (normative)
Determination of aluminum — ICP emission spectrochemical method

1 Summary Decompose a sample with sulfuric acid and nitric acid, heat to generate the white fumes of sulfuric acid, dissolve with hydrochloric acid and filter it. Fuse the insoluble residue with potassium disulfate and dissolve it to filtrate. Nebulize the solution into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of the emitted light.

2 Reagents The reagents shall be as follows:

- a) **Hydrochloric acid (1+1, 1+50)**
- b) **Nitric acid (1+1)**
- c) **Hydrofluoric acid**
- d) **Sulfuric acid (1+1)**
- e) **Potassium disulfate**
- f) **Molybdenum (powder)** High purity molybdenum, which contains no aluminum or the known content as low as possible.
- g) **Iron** High purity iron, which contains no aluminum or the known content as low as possible.
- h) **Yttrium solution (1 mg Y/ml)** Add 50 ml of hydrochloric acid (1+1) to 1.269 9 g of yttrium oxide (III) [purity at least 99.9 % (*m/m*)] and decompose by heating. After cooling it to the ordinary temperature, transfer the solution into a volumetric flask of 1 000ml and dilute to the marked line with water.
- i) **Aluminum standard solution (0.10 mg Al/ml)** Weigh out 0.100 g of aluminum [at least 99.95% (*m/m*)], transfer it into an Erlenmeyer flask (300 ml), put a funnel into an opening of the flask, add 50 ml of hydrochloric acid (1+1) and heat gradually to decompose it. After cooling to ordinary temperature, transfer the solution into a volumetric flask of 1 000 ml with water and dilute up to the marked line with water.

3 Test portion Weigh out 1.0 g of sample to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of sample The decomposition of sample shall be carried out in accordance with the following procedures.

- a) Weigh out a sample, transfer it into a polytetrafluoroethylene (hereafter referred to as PTFE) beaker (200 ml) or a platinum dish (No. 100).
- b) Cover it, add 10 ml of sulfuric acid (1+1) and then add little by little 20 ml of nitric acid (1+1), decompose by heating and cool it. Wash the bottom side of lid with water and remove it.
- c) Add 5 ml of hydrofluoric acid and heat to generate white fumes of sulfuric acid for about 15 minutes.

- d) After cooling, add about 30 ml of water and 5 ml of hydrochloric acid and heat to dissolve the soluble salts.
- e) Filter the solution through filter paper (Class 5B) and remove the precipitates from the inside wall of beaker using a glass rod with rubber and transfer it onto the filter paper.
- f) Wash the filtrate first with hydrochloric acid (1+50) warmed up to 40 °C to 60 °C until the iron (III) ion can not be detected in the filtrate, then with warm water until acid disappears.
- g) Collect the filtrate and the washings to a beaker (200 ml) and heat to concentrate the filtrate and the washings to about 50 ml.

4.2 Treatment of insoluble residue Treatment of insoluble residue shall be carried out in accordance with the following procedures.

- a) Transfer the insoluble residue obtained in 4.1 f) and the filter paper into a platinum crucible (No. 30) and incinerate the filter paper to ash by heating at a low temperature.
- b) After cooling, moisten the residue in the platinum crucible with 2 or 3 drops of sulfuric acid (1+1), add about 5 ml of hydrofluoric acid and heat to vaporize silicon dioxide and sulfuric acid, taking care not to splash.
- c) After cooling, add 1.0 g of potassium disulfate and cover with a lid. Raise the temperature gradually, heat the crucible at about 700 °C and fuse the residue perfectly.
- d) After cooling, put the platinum crucible and the lid into the solution obtained in 4.1 g).
- e) Heat gently to dissolve the melt, wash the platinum crucible and lid with water, and remove it.
- f) After cooling down to ordinary temperature, transfer it to a measuring flask of 100 ml with water.

4.3 Preparation of the solution for measuring the emitted intensities Preparation of the solution for measuring the emitted intensities shall be in accordance with either one of the following methods.

- a) **For the application of the emitted intensities method** Dilute the solution obtained in 4.2 f) to the marked line with water.
- (b) **For the application of the intensities ratio method** After adding accurately 10 ml of yttrium solution [2 h)] to the solution obtained in 4.2 f), and dilute the volume to the marked line with water.

4.4 Measurements of the emitted intensities Measurements of the emitted intensities shall be in accordance with either one of the following methods (¹).

- a) **For the application of the emitted intensities method** Nebulize a part of the solution obtained in 4.3 a) into an argon plasma of ICP emission spectrochemical analyzer and measure the intensity of aluminum at 237.34 nm in wavelength.
- b) **For the application of the intensities ratio method** Nebulize a part of the solution obtained in 4.3 b) into an argon plasma of ICP emission spectrochemical analyzer and

measure the intensity of aluminum at 237.34 nm in wavelength and that of yttrium at 371.03 nm in wavelength. Calculate the ratio of aluminum intensity to yttrium intensity.

Note (1) Fundamental operation of measurement shall be in accordance with 5 in JIS K 0116.

5 Blank test The emitted intensity or intensity ratio measured in the solution to which copper standard solution is not added in the preparation of the working curve of 6 is used as that of blank test.

6 Preparation of working curve Preparation of working curve shall be carried out in accordance with the following procedures in parallel with the determination of the sample.

- a) Weigh out 0.60 g of molybdenum [2 f)] and 0.40 g of iron [2 g)], transfer them into several PTFE beakers (200 ml) or platinum dishes (No. 100).
- b) Carry out the same operation as in the sample in accordance with the procedures of 4.1 b) to 4.2 f).
- c) Add correctly stepwise 0 ml to 20 ml of standard aluminum solution [2 i)] gradually (corresponding to 0 mg to 2.0 mg of aluminum).
- d) Hereafter, carry out the same operation as in the sample in accordance with the procedures of 4.3 and 4.4.
- e) Prepare the correlation curve between the emitted intensity or intensity ratio obtained and total amounts of aluminum content added as the aluminum standard solution and aluminum content in molybdenum and iron. Use this correlation curve as working curve.

7 Calculation Aluminum content in sample shall be calculated in accordance with the following formula.

$$Al = \frac{A - B}{m} \times 100 + C$$

where *Al*: aluminum content in the sample [% (m/m)]

A : etected amount of aluminum in sample solution (g)

B : detected amount of aluminum in blank test solution (g)

m : test portion (g)

C : weighted total of aluminum content in molybdenum [2 f)] and iron [2 g)] used in blank test, which shall be calculated in accordance with the following formula

$$C = a \times 0.60 + b \times 0.40$$

where *a* : aluminum content in molybdenum [2 f)] [% (m/m)]

b : aluminum content in iron [2 g)] [% (m/m)]

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Standardization Promotion Department, Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN
TEL. 03-3583-8002 FAX. 03-3583-0462