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Method for chemical analysis of ferrotungsten

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Foreword

This translation has been 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. And **JIS Z 9022:1959** and **JIS Z 9023:1963** were withdrawn and also replaced with this revision.

This revision has been made based on **ISO 8258:1991** *Shewhart control charts*, as the 1st edition and Technical Corrigendum 1 of **ISO 8258** published in 1993 without changing the technical contents.

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Method for chemical analysis of ferrotungsten

Introduction When a standard is applied, standards which are cited in this Standard shall be also simultaneously referred to.

Since ferrotungsten is often used as auxiliary raw material, in addition to the methods for determination of ferrotungsten as principal component, the methods for determination of ten components such as carbon or the like coming into problems on manufacture of iron and steel are specified, and JIS G 1316 is enacted in 1953. Annex 2 is Japanese Industrial Standard prepared by translating ISO 7693, *Ferrotungsten—Determination of tungsten content—Gravimetric method* issued as the first edition in 1980 without changing the technical contents and the style of Japanese Industrial Standard.

Further, "Informative reference" with the dotted underline in Annex 2 is an item which does not exist in the original International Standard.

1 Scope This Japanese Industrial Standard specifies the methods for determination of tungsten, carbon, silicon, manganese, phosphorus, sulfur, tin, copper, arsenic, antimony and bismuth in ferrotungsten.

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 K 8005 *Reference materials for volumetric analysis*

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

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

3 General matters General matters common to the determination shall be in accordance with JIS G 1301, JIS K 0116 and JIS K 0121. However, they are not applied to Annex 2.

4 Division of methods for determination The methods for determination of various kinds of components in ferrotungsten shall be as given in Table 1.

Table 1 Methods for determination of various kinds of components in ferrotungsten

Component	Determination method	Applied content range % (m/m)	Annex (normative) number
Tungsten	Cinchonine precipitation separation tungsten (VI) oxide gravimetric method	70 or over up to and incl. 90	1
	Cinchonine and benzoin- α -oxime precipitation separation tungsten (VI) oxide gravimetric method (ISO 7693)	70 or over up to and incl. 90	2
Carbon	Combustion—Gas volumetric method	0.05 or over up to and incl. 3.0	3
	Combustion—Infrared absorption method	0.001 or over up to and incl. 3.0	4
Silicon	Potassium hexafluorosilicate precipitation separation sodium hydroxide titration method	0.2 or over up to and incl. 1.0	5
	Molybdosilicate Blue absorptiometry	0.01 or over up to and incl. 0.50	6
	ICP emission spectroscopy	0.02 or over up to and incl. 1.0	7
Manganese	Permanganate absorptiometry	0.01 or over up to and incl. 0.50	8
	Atomic absorption spectrometry	0.01 or over up to and incl. 2.0	9
	ICP emission spectroscopic analysis	0.01 or over up to and incl. 2.0	10
Phosphorus	Beryllium hydroxide coprecipitation separation molybdophosphate blue absorptiometry	0.002 or over up to and incl. 0.10	11
	Beryllium hydroxide coprecipitation separation ICP emission spectroscopic analysis	0.002 or over up to and incl. 0.10	12
Sulfur	Combustion—Sodium hydroxide titration method	0.005 or over up to and incl. 1.0	13
	Combustion—Infrared absorption method	0.001 or over up to and incl. 1.0	14
Tin	Sulfide precipitation and manganese dioxide coprecipitation separation phenylfluorone absorptiometry	0.002 or over up to and incl. 0.10	15
	Iodide extraction atomic absorption spectrometry	0.002 or over up to and incl. 0.10	16
Copper	Atomic absorption spectrometry	0.001 or over up to and incl. 0.10	17
	ICP emission spectroscopy	0.001 or over up to and incl. 0.10	18
Arsenic	Molybdoarsenic blue absorptiometry	0.002 or over up to and incl. 0.10	19
Antimony	Sulfide precipitation, manganese dioxide coprecipitation and chloride extraction separation rhodamine B absorptiometry	0.001 or over up to and incl. 0.06	20
	Iodide extraction atomic absorption spectrometry	0.001 or over up to and incl. 0.03	21

Table 1 (concluded)

Component	Determination method	Applied content range % (m/m)	Annex (normative) number
Bismuth	Sulfide precipitation and iron hydroxide coprecipitation separation iodide absorptiometry	0.015 or over up to and incl. 0.05	22
	Sulfide precipitation and iron hydroxide coprecipitation separation iodide extraction absorptiometry	0.001 or over up to and incl. 0.015	23
	Iodide extraction atomic absorption spectrometry	0.000 5 or over up to and incl. 0.015	24

Annex 1 (normative)**Method for determination of tungsten—
Cinchonine precipitation separation tungsten (VI) oxide
gravimetric method**

1 Summary Decompose a sample with nitric acid and hydrofluoric acid, add sulfuric acid, generate white fumes of sulfuric acid by heating, almost dry up or fuse the sample with sodium peroxide and sodium carbonate. Dissolve in hydrochloric acid, add cinchonine, generate the precipitate of tungsten, filter, ignite, and weigh the mass of tungsten (VI) oxide containing impurities. Fuse the tungsten (VI) oxide containing impurities with sodium carbonate, dissolve in warm water, filter undissolved residue, ignite, and weigh the mass.

2 Reagents The reagents shall be as follows.

- a) **Hydrochloric acid**
- b) **Hydrochloric acid (1+1)**
- c) **Nitric acid (1+1)**
- d) **Hydrofluoric acid**
- e) **Sulfuric acid (1+1)**
- f) **Aqueous ammonia**
- g) **Sodium peroxide**
- h) **Sodium carbonate**
- i) **Ammonium thiocyanate solution (50 g/l)**
- j) **Tin (II) chloride solution** Dissolve 350 g of tin (II) chloride dihydrate in 100 ml of hydrochloric acid (1+1) by heating. After cooling, dilute the solution to 1 000 ml with water.
- k) **Iron (III) sulfate solution** Dissolve 8 g of iron (III) sulfate *n*-hydrate with 1 ml of sulfuric acid (1+1) and a small amount of water, and dilute the solution to 100 ml with water.
- l) **Citric acid**
- m) **Cinchonine solution** Dissolve 100 g of cinchonine in 1 000 ml of hydrochloric acid (1+1).
- n) **Cinchonine washing solution** Add water to 30 ml of cinchonine solution [2 m)] to dilute the liquid to 1 000 ml.
- o) **Ethyl acetate**

3 Weighing-out amount of sample The weighing-out amount of a sample shall be 0.50 g, and read to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of sample and generation of precipitate The decomposition of a sample and the generation of a precipitation shall be carried out according to either of the following procedures.

a) In the case where a sample is easily decomposed with nitric acid and hydrofluoric acid

- 1) Weigh out a sample, transfer onto a platinum dish (no. 150), and cover it.
- 2) Add 10 ml of nitric acid (1+1), and decompose by dripping 5 ml of hydrofluoric acid.
- 3) Wash the under surface of the cover with water, remove it, add 5 ml of sulfuric acid (1+1), and concentrate until white fumes of sulfuric acid is hardly generated by heating gently so as not to bump.
- 4) After allowing to cool, add 10 ml of hydrochloric acid and 30 ml of warm water, dissolve soluble salts by gentle heating so as not to bump, and transfer into a beaker (300 ml) by washing with warm water.
- 5) Dissolve tungstic acid adhering to the platinum dish by dripping a small amount of aqueous ammonia. After making the solution acidic by adding 10 ml of hydrochloric acid (1+1), combine it into the solution obtained in 4) and dilute the solution to about 150 ml by adding warm water.
- 6) Add 5 ml of cinchonine solution [2 m] to the solution, after boiling for several min by heating, keep it at about 90 °C for 30 min, and allow to stand in a warm place for about 3 h.

b) In the case where a sample is difficult to be decomposed with acid

- 1) Weigh out a sample, and transfer into a nickel crucible (no. 30).
- 2) Add 6 g of sodium peroxide and 2 g of sodium carbonate, and sufficiently mix.
- 3) Start to heat gently, gradually raise the temperature, and at about 800 °C for 3 min, heat and melt the sample while occasionally shaking the crucible.
- 4) After allowing to cool, transfer the crucible into a beaker (500 ml), and dissolve the melt by adding little by little 150 ml of hydrochloric acid (1+1).
- 5) Wash the crucible with water, remove it, and take the solution in the beaker as the principal solution.
- 6) Dissolve tungstic acid adhering to the crucible by dripping a small amount of aqueous ammonia. After making it acidic by adding hydrochloric acid (1+1), combine it into the principal solution obtained in 5), and concentrate by heating until the solution amount becomes about 70 ml.
- 7) Add 5 ml of cinchonine solution [2 m] to the solution, dilute the solution to about 300 ml by adding warm water. After boiling for several min by heating, keep it at about 90 °C for 30 min, and allow to stand in a warm place for about 3 h.

4.2 Filtration of precipitate Filter the precipitate according to the following procedure.

- a) Filter the precipitate obtained in **a) 6)** or **b) 7)** of **4.1** by using filter paper (class 5C).
- b) Rub out the precipitate adhering to the beaker with a policeman (a glass rod with rubber), and transfer onto filter paper⁽¹⁾.
- c) Wash the surface of the filter paper with cinchonine washing solution [**2 n**] until iron (III) ion is not observed in washings.

Note ⁽¹⁾ In the case where tungstic acid stuck to the beaker can not completely be detached, wipe off with the filter paper (class 5A) moistened with aqueous ammonia, and mix it into the platinum crucible of **4.3 a)**.

4.3 Weighing amount of tungsten (VI) oxide containing impurities Weigh tungsten (VI) oxide containing impurities according to the following procedure.

- a) Put the precipitate obtained in **4.2 c)** together with the filter paper into a platinum crucible (no. 30).
- b) After drying, incinerate the filter paper by heating at low temperature⁽²⁾.
- c) Ignite by raising temperature to 750 °C to 800 °C⁽³⁾.
- d) After allowing to cool to ordinary temperature in a desiccator, measure the mass.
- e) Repeat the operations of **c)** and **d)** to constant mass.

Notes ⁽²⁾ When the sample is operated in accordance with **4.1 b)**, after incinerating the filter paper at low temperature, allow to cool, moisten the residue with 2 to 3 drops of sulfuric acid (1+1), add about 5 ml of hydrofluoric acid, and vaporize silicon dioxide and sulfuric acid by heating.

⁽³⁾ Since tungsten (VI) oxide may be distilled by igniting at high temperature, do not ignite at over 800 °C.

4.4 Weighing of impurities Weigh impurities according to the following procedure.

- a) Add about 10 g of sodium carbonate into the platinum crucible made to constant mass in **4.3 e)**, sufficiently mix, and melt by heating.
- b) After allowing to cool, transfer the platinum crucible containing the melt into a beaker (300 ml), add about 150 ml of warm water to dissolve the melt, wash the platinum crucible with warm water, take it out, and store it.
- c) Filter the solution in the beaker with filter paper (class 5B), and wash sufficiently the residue on the filter paper with warm water⁽⁴⁾.
- d) Transfer the residue together with the filter paper into the platinum crucible stored in **b)**, dry, and incinerate the filter paper at low temperature.
- e) Raise temperature to 750 °C to 800 °C, and ignite.
- f) After allowing to cool to ordinary temperature in the desiccator, measure the mass.

- g) Repeat the operations of e) and f) to constant mass.

Note (4) In the case where molybdenum may be contained in the sample, store the filtrate and washings.

4.5 Determination of molybdenum⁽⁵⁾ Determine molybdenum according to the following procedure.

- a) Transfer the filtrate and washings stored in Note (4) into a 250 ml one-mark volumetric flask. After cooling to ordinary temperature, dilute to the mark with water. Partially take 5 ml from the solution, and transfer into a separatory funnel (200 ml).
- b) Dissolve by adding 1 g of citric acid. After making the solution slightly acidic by dripping sulfuric acid (1+1), add 25 ml of iron (III) sulfate solution [2 k)], shake, add 10 ml of ammonium thiocyanate solution, and shake. Further add 10 ml of tin (II) chloride solution [2 j)], shake, and color molybdenum. Thereafter, add accurately 25 ml of ethyl acetate, vigorously shake for about 1 min, extract thiocyanate complex of molybdenum into the organic phase, and discard the lower aqueous solution layer. Filter the organic phase with dry filter paper (class 5A), transfer a portion of that into the absorption cell (10 mm) of a photometer, and measure absorbance near 460 nm wavelength by taking ethyl acetate as contrast solution.
- c) **Preparation of working curve** Add, sampling by stages, standard molybdenum solution into a plurality of separatory funnels (200 ml), hereafter carry out the operation of b) parallel to the sample, and prepare the relation curve between the obtained absorbance and the molybdenum amount added as standard molybdenum solution to prepare the working curve.
- d) Obtain the molybdenum amount in sample solution from the absorbance obtained in b) and the working curve prepared in c).

Note (5) Carry out the operation only in the case where molybdenum may be contained in the sample.

5 Blank test The blank test is not carried out.

6 Calculation Calculate according to either of the following procedures.

- a) **In the case where the operation of 4.5 is not carried out** Calculate the tungsten content in the sample according to the following formula.

$$W = \frac{(m_1 - m_2) \times 0.7930}{m} \times 100$$

where, W: tungsten content in sample [% (m/m)]

m_1 : mass obtained in 4.3 c) (g)

m_2 : mass obtained in 4.4 g) (g)⁽⁵⁾

m : weighed-out amount of sample (g)

- b) **In the case where the operation of 4.5 is carried out** Calculate the tungsten content in sample according to the following formula.

$$W = \frac{m_1 - \left(m_2 \times A \times \frac{250}{5} \times 1.5 \right)}{m_0} \times 100$$

where, W : tungsten content in sample [% (m/m)]

m_1 : mass obtained in **4.3 c)** (g)

m_2 : mass obtained in **4.4 g)** (g)

A : molybdenum detected amount obtained in **4.5 d)** (g)

m_0 : weighed-out amount of sample (g)

Annex 2 (normative)
**Method for determination of tungsten—Cinchonine and
benzoin- α -oxime precipitation separation tungsten (VI)
oxide gravimetric method (ISO 7693)**

1 Scope and field of application This Annex 2 specifies a cinchonine gravimetric method for the determination of the tungsten content of ferrotungsten.

It also specifies, in the supplement to annex, a spectrometric method for the determination of molybdenum which interferes with the determination.

The method is applicable to ferrotungsten having tungsten contents between 70 % (m/m) to 90 % (m/m).

2 Reference

ISO 3713 *Ferroalloys—Sampling and preparation of samples—General rules*¹⁾

Informative reference : Though “at present at the stage of draft” is stated as footnote ¹⁾ in the original, the ISO 3713 was issued in 1987.

3 Principle Dissolution of a test portion using hydrofluoric, nitric and sulphuric acids. Evaporation of the solution until copious white fumes are evolved.

Separation and fusion of the residue with sodium carbonate and diboron trioxide. Dissolution of the fused residue in hot water.

Precipitation of the tungsten with cinchonine and α -benzoin oxime, ignition of the precipitate and weighing of the impure tungstic (VI) oxide. Purification of the impure tungstic (VI) oxide by fusion with sodium carbonate, dissolution in hot water, filtration and recovery of the insoluble impurities. Spectrometric determination of molybdenum (see the supplement to annex).

Determination of the tungsten content from the difference between the mass of the impure tungstic (VI) oxide and that of the impurities.

Informative reference : Though only “the impure tungsten oxide” is stated in the original, since the valance of tungsten in this case is 6-valent, that is clarified by adding (VI).

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

4.1 Sodium carbonate

4.2 Acetone

4.3 Diammonium hydrogen citrate $[(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7]$

4.4 Diboron trioxide (B_2O_3)

4.5 Nitric acid ρ 1.40 g/ml, approximately 14 mol/l solution

4.6 Hydrofluoric acid ρ 1.16 g/ml, approximately 48 % (m/m) solution

4.7 Hydrochloric acid ρ 1.19 g/ml, approximately 12 mol/l solution

4.8 Ethanol ρ approximately 0.790 g/ml

4.9 Sulphuric acid, diluted 1+1

Carefully add 1 volume of sulphuric acid (ρ 1.84 g/ml, approximately 18 mol/l solution) to 1 volume of water and mix thoroughly whilst cooling.

4.10 Hydrochloric acid, diluted 1+9

Add 1 volume of the hydrochloric acid (4.7) to 9 volumes of water and mix thoroughly.

4.11 Hydrochloric acid, diluted 1+99

Add 1 volume of the hydrochloric acid (4.7) to 99 volumes of water and mix thoroughly.

4.12 Ammonium hydroxide, diluted 1+1

Add 1 volume of ammonium hydroxide (ρ 0.885 g/ml, approximately 32 % (m/m) solution) to 1 volume of water and mix thoroughly.

4.13 Ammonium chloride, 20 g/l solution

Dissolve 2 g of ammonium chloride in water, dilute to 100 ml and mix thoroughly.

4.14 Cinchonine, 125 g/l solution

Dissolve 125 g of cinchonine in hydrochloric acid (4.7) diluted 1+1, and complete to 1 000 ml with that acid.

4.15 α -benzoin oxime, 30 g/l solution

Dissolve 3 g of α -benzoin oxime in 95 ml of acetone (4.2). Transfer to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

4.16 Cinchonine/ α -benzoin oxime, wash solution

Place 10 ml of the cinchonine solution (4.14), 5 ml of the α -benzoin oxime solution (4.15) and 2.5 ml of the hydrochloric acid (4.7) in a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

4.17 Ammonium thiocyanate, 100 g/l solution

Dissolve 100 g of ammonium thiocyanate in water, dilute to 1 000 ml and mix thoroughly.

4.18 Tin (II) chloride, 200 g/l solution in hydrochloric acid (4.7) diluted 1+1

Dissolve 40 g of tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 150 ml of hydrochloric acid (4.7) diluted 1+1. Heat gently, cool, dilute to 200 ml with more of the hydrochloric acid diluted 1+1 and mix thoroughly.

Prepare this solution immediately before use.

4.19 Phenolphthalein, 1 g/l solution in the ethanol (4.8) solution**5 Apparatus**

Usual laboratory equipment and in particular.

5.1 Spectrophotometer⁽¹⁾, with selector for continuous variation of wavelength, or

5.2 Spectrometer⁽¹⁾, with selector for discontinuous variation of wavelength, equipped with appropriate filters giving maximum transmission at a wavelength of 460 nm.

5.3 Cells⁽¹⁾, of thickness 1 (or 2) cm.

Note ⁽¹⁾ These are required for the determination of molybdenum (see the supplement to annex) when the molybdenum content of the sample is not known.

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

7 Procedure

7.1 Test portion Take a test portion of (1 ± 0.001) g.

7.2 Blank test Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents, but omitting the test portion.

7.3 Control test Check the validity of the operating procedures used by carrying out, in parallel with the determination and following the same procedure, determination(s) of the tungsten content(s) of one or several samples of the same type, having known tungsten content(s).

7.4 Determination

7.4.1 Dissolution Place the test portion in a 60 ml platinum crucible fitted with a platinum lid and add 5 ml of the hydrofluoric acid (4.6). Add the nitric acid (4.5) carefully, drop by drop, and heat to light boiling until decomposition of the test portion is complete.

Remove from the source of heat and rinse the sides of the crucible and the lid with water. Add 15 ml of the sulphuric acid solution (4.9) and heat carefully on a sand-bath until copious white fumes are evolved.

Allow to cool, and then dissolve the soluble salts in 10 ml of the hydrochloric acid (4.7) and 30 ml of hot water.

7.4.2 Filtration of impure tungstic oxide Filter the contents of the 60 ml platinum crucible on a fine-grained ashless filter paper, collecting the filtrate in a 600 ml beaker. Wash the filter and the precipitate with the hydrochloric acid solution (4.10).

Dissolve the precipitate [essentially tungstic (VI) acid] in the smallest possible quantity of ammonium hydroxide solution (4.12), then wash the filter with the ammonium chloride solution (4.13). Collect the solution resulting from dissolution and washing with the filtrate in the 600 ml beaker.

7.4.3 Treatment of any insoluble residue remaining on the filter Transfer the filter with any insoluble residue to the original 60 ml platinum crucible. Dry and ignite the filter, heating the residue at a temperature below 750 °C. Cool, add 0.5 g of the sodium carbonate (4.1) and 0.5 g of the diboron trioxide (4.4). Heat over a burner, gently at first, and then more strongly, until the mixture just fuses. Cool, and then dissolve the fused material in hot water. Filter the solution obtained on a fine-grained filter paper, collecting the filtrate in the same 600 ml beaker (see 7.4.2). Wash the filter with hot water.

7.4.4 Precipitation of tungsten

7.4.4.1 Neutralize the solution in the 600 ml beaker by adding 10 ml in excess of the hydrochloric acid (4.7). Boil for 5 min. Remove the beaker from the source of heat and dilute the contents to approximately 450 ml with hot water. Add 30 ml of the cinchonine solution (4.14) and a small amount of ashless filter paper pulp, and allow the solution to stand for 30 min at 90 °C, agitating it from time to time. Then allow the solution to stand at ambient temperature for at least 4 h or, preferably, overnight.

7.4.4.2 Add 5 ml of the α -benzoin oxime solution (4.15) and agitate vigorously for a few minutes. Allow to stand for 1 h at ambient temperature. Filter using a conical filter funnel with an 11 cm diameter filter paper containing a little ashless filter paper pulp.

Wash three times by decantation, then with the hot cinchonine/ α -benzoin oxime solution (4.16) and then several times with cold hydrochloric acid solution (4.11). Finally wash with cold water.

Transfer the filter containing the precipitate to a tared platinum crucible and heat carefully to complete incineration. Add a few drops of the nitric acid (4.5) and evaporate to dryness on a sand-bath. Ignite the tungstic (VI) oxide (for approximately 30 min) at a temperature not exceeding 750 °C⁽²⁾ in an electric muffle furnace until constant mass is attained.

Allow to cool in a desiccator and weigh the crucible containing the impure tungstic (VI) oxide.

Note (2) The temperature of 750 °C should not be exceeded, because, at a temperature even slightly higher than this, tungstic (VI) oxide volatilizes slowly and continuously and this may lead to appreciable errors.

7.4.4.3 Add 5 g of the sodium carbonate (4.1) and mix completely with the impure tungstic (VI) oxide. Cover the mixture with 1 g to 2 g of the sodium carbonate (4.1) and heat the mixture until it fuses.

Swirl the crucible to detach the tungstic (VI) oxide adhering to the walls of the crucible to incorporate it with the fused mass. Cool, and dissolve the fused material in hot water. Add some drops of the ethanol (4.8), heat for a few minutes, filter and wash the crucible and residue with hot water, retaining the filtrate (filtrate A). Transfer the filter containing the residue to the crucible and ignite; add 1 g to 2 g of the sodium carbonate (4.1) [Informative reference : Though (4.11) is stated in the original paper, (4.1) is correct.] and again fuse.

Dissolve the fused mass in water, add some drops of the ethanol (4.8), filter and wash the residue thoroughly to remove the sodium carbonate completely (filtrate B). Combine filtrate A with filtrate B in order to determine the molybdenum content (see the supplement to annex) if required.

Place the filter containing the residue in the crucible, ignite, at a temperature not exceeding 750 °C in the electric muffle furnace. Allow to cool and weigh.

8 Expression of results The tungsten content, expressed as percentage by mass, is given by the formula

$$\frac{0.7930 [(m_1 - m_2) - (m_3 - m_4)] \times 100}{m_0}$$

where, m_0 : the mass, in grams, of the test portion

m_1 : the mass in grams, of the impure tungstic (VI) oxide (see 7.4.4.2)

m_2 : the mass, in grams, of the residue obtained after fusion with sodium carbonate (see 7.4.4.3)

m_3 : the mass, in grams, of the impure tungstic (VI) oxide in the blank test (see 7.2)

m_4 : the mass, in grams, of the residue obtained after fusion with sodium carbonate in the blank test (see 7.2)

0.7930: the conversion factor to express the tungstic (VI) oxide content as the tungsten content

9 Test report The test report shall include the following information:

- a reference to this Annex 2;
- identification of the sample;
- the result and the method of expression used;
- any unusual features noted during the determination;
- details of any operations not specified in this Annex 2 or regarded as optional.

Supplement to Annex

Determination of molybdenum

A.1 General The tungstic (VI) oxide obtained may contain traces [some hundredths of 1 % (*m/m*)] of molybdenum in the form of molybdic (VI) oxide. If the molybdenum content is not known, it is necessary to determine it spectrometrically and to correct the mass of tungstic (VI) oxide.

A.2 Procedure Boil the combined filtrate (A+B) to concentrate the solution to a volume of approximately 80 ml. Transfer the solution to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

Transfer a 10 ml aliquot portion of this solution, containing not more than 0.30 mg of molybdenum, to a 50 ml one-mark volumetric flask. Add 2 g of the diammonium hydrogen citrate (4.3) and agitate until dissolution is complete. Add 3 drops of the phenolphthalein solution (4.19), the hydrochloric acid (4.7) until the red coloration is eliminated, and then 5 ml of the hydrochloric acid in excess. Add, agitating after each addition, 5 ml of the ammonium thiocyanate solution (4.17), 20 ml of the acetone (4.2) and 7 ml of the tin (II) chloride solution (4.18). Dilute to the mark with acetone and mix thoroughly.

Carry out the spectrometric measurements on the solution, using the spectrometer (5.1) set a wavelength of approximately 460 nm, or the spectrometer (5.2) equipped with the appropriate filters. (Cells of thickness 1 cm are generally used.)

Carry out the measurements within a period not exceeding 15 min after coloration. Determine the molybdenum content from the calibration graph and (see clause A.3) and subtract the mass of molybdic (VI) oxide thus obtained from the mass of the impure tungstic (VI) oxide.

A.3 Preparation of the calibration graph Prepare standard matching solutions by placing varying amounts of standard molybdenum solutions (corresponding to 0.050 mg and 0.010 mg of Mo per litre) into a series of six 50 ml one-mark volumetric flasks. Add to the contents of each flask 2 g of the diammonium hydrogen citrate (4.3) and agitate until dissolution is complete. Proceed as described in clause A.2, second paragraph, from "Add 3 drops of the phenolphthalein solution (4.19) ...".

Plot a graph having, for example, the measured absorbances as ordinates and the corresponding molybdenum contents as abscissae.

Annex 3 (normative)
Method for determination of carbon—
Combustion-Gas volumetric method

1 Summary Heat a sample at high temperature in an oxygen gas flow, and oxidize carbon to carbon dioxide. Collect it together with oxygen in a burette, measure the volume of the gas, then remove carbon dioxide by absorbing in alkali solution, and measure the volume of the residual gas.

2 Apparatus The apparatus shall be as given in 6.3.2 Attached Fig. 2 of 6.3 in JIS Z 2615.

3 Devices and materials The devices and materials shall be in accordance with 5 of JIS Z 2615.

4 Weighing-out amount of sample The weighing-out amount of a sample shall be as specified in Annex 3 Table 1 and read to the nearest 0.1 mg.

Annex 3 Table 1 Weighing-out amount of sample

Carbon content % (m/m)	Weighing-out amount of sample g
0.05 or over to and excl. 0.3	2.0
0.3 or over to and excl. 1.0	1.0
1.0 or over up to and incl. 3.0	0.50

5 Operation

WARNING FOR SAFETY: In burning operation, cares shall be taken for treatment of a porcelain combustion boat or a porcelain combustion crucible which is heated at high temperature so as not to burn by necessarily using crucible tongs or the like.

Further, an effort shall be made for prevention from generation of a fire by taking care of treatment of exhaust of excess oxygen.

5.1 Preparatory operation The preparatory operation shall be as given in 6.3.3 of 6.3 in JIS Z 2615. However, in the case of using a tubular electric resistance heating furnace, a temperature in the combustion tube shall be 1 400 °C to 1 450 °C⁽¹⁾.

Further, in the case of using a high frequency induction heating furnace, conditions concerning to high frequency induction heating shall be set⁽²⁾.

Notes (1) Correct with care for a difference in temperature between temperature indication of a pyrometer and temperature in the combustion tube.

(2) The conditions herein mean, for example, conditions determined according to the specification of apparatus using the anode current and grid current of high frequency oscillator or the like.

5.2 Determination operation Carry out the determination operation according to either of the following procedures⁽³⁾.

Note ⁽³⁾ In ordinary operations, carry out necessarily the same operation as that for the analytical sample by using the sample of a known carbon content at initial, middle, and final periods of the operation time, and examine whether or not the apparatus and others are functioning normally.

a) In the case of using tubular electric resistance heating furnace

- 1) Weigh out a sample, and transfer into a porcelain combustion boat⁽⁴⁾.
- 2) Open the inlet part of the combustion tube of tubular electric resistance furnace, insert the porcelain combustion boat containing the sample into the combustion tube to its center part, and immediately stopper airtightly.
- 3) Open the three-way cock (f) to the furnace side, and allow to stand for about 2 min regulating the feed amount of oxygen.
- 4) Hereafter, operate in accordance with the procedure of (2) to (6) of 6.3.4 of 6.3 in JIS Z 2615.

Note ⁽⁴⁾ Select the optimum fuel additive from those given in 5 (13) of JIS Z 2615 (for example, tin, copper, iron, tungsten, etc.), add the fuel additive of 2 times to 4 times the amount of the sample, sufficiently mix into the weighed out sample, or cover the sample therewith.

b) In the case of using high frequency induction heating furnace

- 1) Weigh out a sample, and transfer into the porcelain combustion crucible⁽⁴⁾.
- 2) Connect the apparatus. After conforming airtightness, close the three-way cock (m), and open the three-way cock (l) to the open air side.
- 3) Place the porcelain combustion crucible containing the sample obtained in 1) on a receiving base of the high frequency induction heating furnace, insert into the central part of a heating coil by operating an operation handle, and close the combustion tube.
- 4) Feed oxygen, and replace air in the combustion tube therewith.
- 5) Close the three-way cock (l), and function the high frequency induction furnace.
- 6) After 10 s to 20 s has elapsed, open the three-way cock (m) to the furnace side, then slightly open the three-way cock (l) to the furnace side, and conduct gradually combustion gas through desulfurization tube (j) and condenser tube (k) to the buret (n).
- 7) After about 1 min has elapsed and the sample is almost completed to be burnt, collect the mixed gas rapidly near to the bottom part of the graduation of the buret (n).
- 8) Close the three-way cock (l) and the three-way cock (m), stop high frequency induction heating, and allow to stand for about 1 min. Hereafter, operate according to the procedure of (4) to (6) of 6.3.4 of 6.3 in JIS Z 2615.

6 Blank test A blank test shall be in accordance with **6.3.5** of **6.3** in **JIS Z 2615**. However, in the case of using high frequency induction heating furnace, since high frequency is not induced only with a blank porcelain combustion crucible, the blank test is carried out by using the same amount of an iron and steel sample of which the carbon content is as low as possible and known as that of the sample, and the carbon amount obtained by subtracting the carbon amount of the iron and steel sample of the known carbon content used for the blank test from the carbon amount obtained in the blank test, is made the blank test value.

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

Annex 4 (normative)
Method for determination of carbon—
Combustion-Infrared absorption method

1 Summary A sample is heated at high temperature in an oxygen gas flow, and carbon is oxidized to carbon dioxide and carbon monoxide. Those together with oxygen are sent to an infrared absorption cell, and the infrared absorption amount with carbon dioxide and carbon monoxide is measured.

2 Apparatus The apparatus shall be in accordance with 6.9.3 of 6.9 or 6.10.2 of 6.10 in JIS Z 2615. However, for the sample combustion part in the integral method, a tubular electric resistance heating furnace can be also used.

3 Devices and materials The devices and materials shall be in accordance with 5 of JIS Z 2615.

4 Weighing-out amount of sample The weighing-out amount of sample shall be the optimum amount for the apparatus used, and read to the nearest 0.1 mg.

Informative reference : The weighing-out amount of a sample shall be generally 0.50 g or 1.0 g.

5 Operation

WARNING FOR SAFETY : In burning operation, cares shall be taken for treatment of a porcelain combustion boat or a porcelain combustion crucible which is heated at high temperature so as not to burn by necessarily using crucible tongs or the like.

Further, an effort shall be made for prevention from generation of a fire by taking care of treatment of exhaust of excess oxygen.

5.1 Preparing operation The preparing operation shall be as given in 6.9.4 of 6.9 or 6.10.3 of 6.10 in JIS Z 2615. However in the case of using a tubular electric heating furnace, a temperature in the combustion tube shall be 1 400 °C to 1 450 °C.

5.2 Determination operation The determination operation shall be carried out according to any one of the following procedures⁽¹⁾.

Note ⁽¹⁾ In ordinary operation, necessarily carry out the same operation as that for the test portion with a sample of a known carbon content at initial, middle, and final periods of the operation time, and check whether or not the apparatus and others are regularly functioning.

a) In the case of integral method using tubular electric resistance heating furnace

- 1) Weigh out a sample, and transfer into a porcelain combustion boat.
- 2) Weigh out accurately 1 g to 2 g of fuel additive⁽²⁾, and place it on the sample in the porcelain combustion tube of 1).

- 3) Open the inlet part of the combustion tube, insert the porcelain combustion boat containing the sample and the fuel additive into a suitable part of the combustion tube, and stopper immediately airtightly.
 - 4) Make an appropriate amount of oxygen flow, and send in the generated combustion generation gas together with oxygen into an infrared detector.
 - 5) Read the integrated value of the infrared absorption amount equivalent to the contents of carbon dioxide and carbon monoxide in the combustion generated gas as the indication value.
- b) **In the case of integral method using high frequency induction heating furnace**
- 1) Weigh out a sample, and transfer into a porcelain combustion crucible.
 - 2) Weigh out accurately 1 g to 2 g of fuel additive⁽³⁾, and place it on the sample in the porcelain combustion crucible in 1).
 - 3) Place the porcelain combustion crucible containing the sample and fuel additive on the receiving base of a high frequency induction heating furnace, insert into the central part of a heating coil, and close the combustion tube.
 - 4) Hereafter, operate according to the procedure of 6.9.5 (2) and (3) of 6.9 in JIS Z 2615.
- c) **In the case of circulation method using high frequency heating furnace**
This method shall be according to the procedure of 6.10.4 of 6.10 in JIS Z 2615.
- Notes (2) For the fuel additive, copper or tin is preferably used, and for its use amount, the optimum amount for the apparatus to be used is preliminarily investigated.
- (3) For the fuel additive, equivalent mixture of tungsten and tin or copper is preferably used. For the use amount, the optimum amount for the apparatus to be used is preliminarily investigated.

6 Blank test Carry out a blank test parallel to the sample by using only the same amount of a fuel additive as that to be added to a sample.

7 Calculation The calculation shall be as described in 6.9.7 of 6.9 or 6.10.6 of 6.10 in JIS Z 2615.

Annex 5 (normative)**Method for determination of silicon—
Potassium hexafluorosilicate precipitation separation
sodium hydroxide titration method**

1 Summary Decompose a sample with nitric acid and hydrofluoric acid coexisting with potassium fluoride, precipitate potassium hexafluorosilicate, filter, dissolve in warm water, and titrate with sodium hydroxide standard solution using phenolphthalein as an indicator.

2 Reagents The reagents shall be as follows. However, potassium fluoride solution, potassium nitrate solution, and 0.05 mol/l sodium hydroxide standard solution shall be stored in a polyethylene-made container.

- a) **Nitric acid**
- b) **Potassium fluoride solution** Add little by little 60 g of potassium fluoride (anhydrous) into 400 ml of hydrofluoric acid cooling that, and dissolve stirring that. After allowing to stand for one night, filter with filter paper (class 5A) by using a polyethylene-made funnel, and use the filtrate.
- c) **Potassium nitrate solution (50 g/l)** Since this solution sometimes presents alkaline, neutralize in such the case.
- d) **Tungsten (powder)** The tungsten having as high purity as possible without containing silicon, or of which the silicon content is as low as possible and known.
- e) **Iron** The iron having as high purity as possible without containing silicon, or of which the silicon content is as low as possible and known.
- f) **0.05 mol/l sodium hydroxide standard solution** The preparation and standardization method shall be as described in 4.5 (19.5) of JIS K 8001.
- g) **Phenolphthalein solution** Dissolve 0.5 g of phenolphthalein in 100 ml of ethanol (95).

3 Weighing-out amount of sample The weighing-out amount of a sample shall be 1.0 g and read to the nearest 0.1 mg.

4 Operation

4.1 Decomposition of sample Decompose a sample according to the following procedure.

- a) Weigh out a sample, and transfer onto a platinum dish (no. 150).
- b) Add 10 ml of nitric acid, cover, and decompose by adding little by little 5 ml of potassium fluoride solution [2 b)]⁽¹⁾.

Note (1) When the reaction is violent, decompose cooling with water, and when the decomposition is slow, heat at 50 °C to 60 °C. However, when heated too long, since tungstic acid is sometimes precipitated, cool immediately after the decomposition is completed.

4.2 Generation of precipitate and filtration Carry out the generation of a precipitate and its filtration according to the following procedure.

- a) Allow to stand still for about 20 min cooling the solution obtained in 4.1 b) at 15 °C or under, and precipitate potassium hexafluorosilicate.
- b) Filter the solution containing the precipitate by using a polyethylene-made funnel attached with filter paper (class 5A), to which a small amount of filter paper pulp is added, cooling at 15 °C or lower.
- c) Wash sufficiently the precipitate on the filter paper with potassium nitrate solution [2 c)] cooled to 15 °C or lower⁽²⁾. Discard the filtrate and washings.

Note ⁽²⁾ Wash until test paper does not turn red when the filtrate is dripped onto the blue litmus test paper.

4.3 Titration Carry out the titration according to the following procedure.

- a) Transfer the precipitate obtained in 4.2 c) together with the filter paper into an Erlenmeyer flask (200 ml).
- b) Add about 50 ml of warm water, and crush the filter paper by shaking sufficiently.
- c) After boiling by heating, add three drops of phenolphthalein solution [2 g)], titrate with 0.05 mol/l sodium hydroxide standard solution [2 f)], and take the point wherein the solution turns faint pink color as the end point.

5 Blank test For a blank test, weigh out 0.80 g of tungsten [2 d)] and 0.20 g of iron [2 e)] in place of the sample, and transfer into a platinum dish (no. 150). Hereafter, execute the same operation as that for the sample in parallel to the sample according to the procedure of 4.1 b) to 4.3 c).

6 Calculation For calculation, calculate the silicon content in a sample according to the following formula.

$$Si = \frac{(V_1 \times F - V_2 \times F) \times 0.000\,3511}{m} \times 100 + C$$

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

V_1 : use amount of 0.05 mol/l sodium hydroxide standard solution in sample (ml)

V_2 : use amount of 0.05 mol/l sodium hydroxide standard solution in blank test (ml)

F : factor of 0.05 mol/l sodium hydroxide standard solution

m : weighed-out amount of sample (g)

C : weighted sum of silicon content [% (m/m)] contained in tungsten [2 d)] and iron [2 e)] which are used in blank test, and calculate according to the following formula