

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Atomic
Absorption Spectrochemical
Analysis of Iron and Steel**

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In the event of any doubt arising,
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Methods for Atomic Absorption Spectrochemical
Analysis of Iron and Steel

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1. Scope

This Japanese Industrial Standard specifies methods for atomic absorption spectrochemical analysis of iron and steel. The applicable content range of its components to be determined shall be as prescribed in Table 1.

Table 1. Applicable Content Range

Component	Determination method	Applicable content range(wt%)
Manganese	Acid decomposition direct method	0.03 and over, up to 2.0
Phosphorus	Molybdephosphoric acid extraction method	0.0003 and over, up to 0.010
Nickel	Acid decomposition direct method	0.003 and over, up to 1.0
Chromium	Acid decomposition direct method	0.002 and over, up to 2.0
Molybdenum	Acid decomposition direct method	0.01 and over, up to 1.0
Copper	Acid decomposition direct method	0.003 and over, up to 1.0
Vanadium	Acid decomposition direct method	0.005 and over, up to 1.0
Cobalt	Acid decomposition direct method	0.01 and over, up to 0.50
Titanium	Acid decomposition direct method	0.01 and over, up to 0.50
Aluminium	Acid decomposition direct method	0.005 and over, up to 0.10
	Iron separation method	0.001 and over, up to 0.010
Tin	Iodide extraction method	0.002 and over, up to 0.10
Lead	Acid decomposition direct method	0.01 and over, up to 0.30
	Iodide extraction method	0.0005 and over, up to 0.010
Magnesium	Acid decomposition direct method	0.001 and over, up to 0.10
Calcium	Acid decomposition direct method	0.0005 and over, up to 0.010
Zinc	Acid decomposition direct method	0.005 and over, up to 0.025
	Ammonium tetrahexyl iodide and trioctylamine extraction method	0.0005 and over, up to 0.0060
Bismuth	Iodide extraction method	0.0005 and over, up to 0.015
Antimony	Iodide extraction method	0.0015 and over, up to 0.050
Tellurium	Iodide extraction method	0.0005 and over, up to 0.050

2. General Matters

General matters common to the analysis methods shall be in accordance with JIS G 1201, JIS K 0050, JIS K 0121, and JIS Z 8402.

Applicable Standards and Corresponding International Standards: See page 68.

3. Method for Determination of Manganese

3.1 Determination Method The method for determination of manganese shall be in accordance with acid decomposition direct method. This method shall be applied to the sample of 0.003 wt% and over to 2.0 wt% excluding.

3.2 Acid Decomposition Direct Method

3.2.1 Summary A sample is decomposed with a suitable acid, joined by perchloric acid and white fume of perchloric acid is generated by heating. Salts are dissolved in hydrochloric acid and the solution is filtered. The filtrate is sprayed into an air and acetylene flame of an atomic absorption photometer and the absorbance is measured.

3.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1, 2 + 100)
- (2) Perchloric acid
- (3) Aqua regia (three parts by volume of hydrochloric acid and one part by volume of nitric acid)
- (4) Mixed acid (one part by volume of hydrochloric acid, one part by volume of nitric acid, and two parts by volume of water)
- (5) Iron High pure iron as far as possible having no manganese or a known manganese content, which is as low as possible.
- (6) Standard manganese solution A (400 $\mu\text{g Mn/ml}$) Weigh out 1.000 g manganese (not less than 99.9 wt%), transfer to a beaker (200 ml), cover with a watch glass, add 30 ml of hydrochloric acid and quietly heat to decompose. After cooling to ordinary temperature, transfer it to a 1000 ml one-mark volumetric flask while washing with water and dilute to the marked line with water to prepare stock solution (1.00 mg Mn/ml). Dilute a specific volume of this stock solution to accurately 2.5 volumes at each service to prepare standard manganese solution A.
- (7) Standard manganese solution B (50 $\mu\text{g Mn/ml}$) Dilute a specific volume of standard manganese solution A to accurately 8 volumes to prepare standard manganese solution B. Prepare this solution at each service.
- (8) Standard manganese solution C (10 $\mu\text{g Mn/ml}$) Dilute a specific volume of standard manganese solution B to accurately five volumes to prepare standard manganese solution C. Prepare this solution at each service.

3.2.3 Weighing out Amount of Sample The weighing out amount of a sample shall be as prescribed in Table 2.

Table 2. Weighing out Amount of Sample

Manganese content wt%	Weighing out amount of sample g
0.003 and over, up to 0.010	1.00
0.010 and over, up to 0.10	0.50
0.10 and over, up to 2.0	0.20

3.2.4 Operation

3.2.4.1 Preparation of Sample Solution The preparation of a sample solution shall be in accordance with either of the following methods.

(1) Sample Easy to be Decomposed by Mixed Acid

- (1.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 20 ml of mixed acid and decompose by heating. Add 15 ml of perchloric acid, successively heat and generate white fume of perchloric acid for 5 to 6 min. After standing to cool, add 10 ml of hydrochloric acid (1 + 1) and dissolve salts.
- (1.2) Filter this solution using a filter paper (class 5A)⁽¹⁾ and wash until the yellow of iron (III) chloride is not recognized on the filter paper by using warm hydrochloric acid (2 + 100) and warm water. Transfer the filtrate and washings to a 100 ml one-mark volumetric flask by washing with water. After cooling to ordinary temperature, dilute to the marked line with water. Discard the residue.

- (2) Sample Difficult to Be Decomposed by Mixed Acid Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of aqua regia and decompose by gently heating. Add 15 ml of perchloric acid, successively heat and generate white fume of perchloric acid for five to six min. After standing to cool, add 10 ml of hydrochloric acid (1 + 1) and dissolve salts.

Hereinafter, operate in accordance with the procedures of 3.2.4.1 (1.2).

Note ⁽¹⁾ When there is no fear of disturbing the suction of a sprayer because of no insoluble residue such as silicon dioxide or the like in a sample solution, the operation of filtration may be omitted.

3.2.4.2 Measurement of Absorbance Spray a portion of solution obtained in 3.2.4.1 into an air and acetylene flame of an atomic absorption photometer of which the zero point is regulated by using water and measure the absorbance at a wavelength given in Table 3.

Table 3. Wavelength to Be Measured

Manganese content wt%	Wavelength nm
0.003 and over, up to 0.50	279.5
0.50 and over, up to 2.0	403.1

3.2.5 Blank Test Weigh out the same amount of iron [3.2.5 (5)] as that of a weighed-out sample instead of the sample and hereinafter operate parallel to the sample in accordance with the procedures of 3.2.4.1 to 3.2.4.2⁽²⁾.

Note ⁽²⁾ In this case, carry out the operation of decomposition by the same operation as that of a sample.

3.2.6 Preparation of Working Curve The preparation of a working curve⁽³⁾ shall be as follows:

Prepare seven beakers (200 ml) for each range of manganese content, weigh out the same amount of iron [3.2.2 (5)] as the weighing out amount of a sample given in Table 2, transfer to each of them and then, add accurately standard manganese solution in accordance with Table 4. Hereinafter, operate in accordance with the procedures of 3.2.4.1 to 3.2.4.2⁽²⁾, prepare the relation curve between the absorbance measured parallel to the sample and the amount of manganese, parallel transfer the relation curve so as to pass through the origin and take said relation curve as the working curve.

Table 4. Additional Amount of Standard Manganese Solution

Manganese content wt%	Standard manganese solution to be used	Additional amount of standard manganese solution
0.003 and over, up to 0.010	C [3.2.2 (8)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.010 and over, up to 0.10	B [3.2.2 (7)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.10 and over, up to 0.50	B [3.2.2 (7)]	0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0
0.50 and over, up to 2.0	A [3.2.2 (6)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0

Note ⁽³⁾ A working curve can be prepared by using a standard sample of a known manganese content of which the composition is similar to that of a sample. In that case, not less than three kinds of standard solutions of different manganese contents shall be selected within each manganese content range given in Table 2. These standard solutions are operated in accordance with the procedures of 3.2.4.1 and 3.2.4.2 and the relation curve between the absorbance measured parallel to the sample and the content of manganese is prepared. The solution curve is parallel transferred so as to pass through the origin and is taken as the working curve. In that case, the content of manganese in the sample is calculated by subtracting the manganese content obtained in a blank test from the manganese content obtained for a sample solution by inserting the absorbance obtained in 3.2.4.2 and 3.2.5 into this working curve.

3.2.7 Calculation Insert the absorbance obtained in 3.2.4.2 and 3.2.5 into the working curve prepared in 3.2.6, obtain each manganese amount and calculate the content of manganese in the sample from the following formula:

$$\text{Manganese wt\%} = \frac{A_1 - A_2}{m} \times 100$$

Where, A_1 : detection amount of manganese in sample solution (g)
 A_2 : detection amount of manganese in blank test solution⁽⁴⁾ (g)
 m : weighing out amount of sample (g)

Note ⁽⁴⁾ In the case where manganese is contained in iron used for a blank test, correction is carried out by subtracting the amount of manganese in a weighed-out iron.

3.2.8 Tolerances The tolerance shall be as given in Table 5⁽⁵⁾.

Table 5. Tolerances

Unit: wt%

Manganese content	Tolerance in the same laboratory	Tolerance between different laboratories
0.003 and over, up to 0.50	$D_2 [0.0165 \times (\text{Mn content}) + 0.00035]$	$D_2 [0.0132 \times (\text{Mn content}) + 0.00041]$
0.50 and over, up to 2.0	$D_2 [0.0033 \times (\text{Mn content}) + 0.0061]$	$D_2 [0.0123 \times (\text{Mn content}) + 0.0008]$

Note ⁽⁵⁾ The value of D_2 in the above Table shall be prescribed in Table 4 of JIS Z 8402.

4. Method for Determination of Phosphorus

4.1 Determination Method The method for determination of phosphorus shall be in accordance with molybdophosphoric acid extraction method. This method applies to the sample of 0.0003 wt% or over to and excluding 0.010 wt% in phosphorus content. However, this method shall not be applied to the sample not less than 0.1 wt% in tungsten content.

4.2 Molybdophosphoric Acid Extraction Method

4.2.1 Summary After decomposing a sample with suitable acid, the sample is joined by perchloric acid, heated and white fume of perchloric acid is generated. The concentration of acid is regulated with perchloric acid or nitric acid and molybdophosphoric acid is generated by adding ammonium molybdate. Thereafter, organic phase is extracted with isobutylacetic acid, sprayed into a dinitrogen monoxide and acetylene flame of an atomic absorption photometer and the absorbance of molybdenum combined with phosphorus is measured.

4.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1)
- (2) Nitric acid
- (3) Nitric acid (1 + 1), 1 + 6)
- (4) Perchloric acid
- (5) Perchloric acid (1 + 3, 2 + 100)
- (6) Hydrofluoric acid
- (7) Boric acid
- (8) Mixed acid (one part by volume of hydrochloric acid and one part by volume of nitric acid)
- (9) Iron The iron as pure as possible having no phosphorus or a known phosphorus content which is as low as possible.
- (10) Hydrogen peroxide
- (11) Ammonium iron (II) sulfate solution Add about 70 ml of water and 2 ml perchloric acid to 4 g of ammonium iron (II) sulfate hexahydrate to dissolve, and dilute to 100 ml with water.
- (12) Ammonium molybdate solution A Dissolve 100 g of ammonium heptamolybdate tetrahydrate with about 900 ml of warm water. After cooling to ordinary temperature, dilute to 1 l with water. If precipitate exists, filter.
- (13) Ammonium molybdate solution B Dissolve 240 g of ammonium heptamolybdate tetrahydrate in about 900 ml of warm water. After cooling to ordinary temperature, dilute to 1 l with water. If precipitate exists, filter.
- (14) Isobutylacetic acid
- (15) Standard phosphorus solution (5 $\mu\text{gP/ml}$) Dry at 100°C for about 1 h, weigh out 0.1098 g of potassium dihydrogenphosphate left to cool to room temperature in a desiccator, transfer to a beaker (300 ml) and add about 100 ml of water to dissolve. Thereafter, transfer to a 1000 ml one-mark volumetric flask by washing with water and dilute to the mark with water to prepare stock solution (25 $\mu\text{g P/ml}$). Dilute a specific amount of the stock solution to accurately five volumes to prepare standard phosphorus solution. Prepare this solution at each service.

4.2.3 Weighing out Amount of Sample The weighing out amount of a sample shall be as prescribed in Table 6.

Table 6. Weighing out Amount of Sample

Phosphorus content wt%	Weighing out amount of sample g
0.0003 and over, up to 0.005	1.00
0.005 and over, up to 0.010	0.50

4.2.4 Operation

4.2.4.1 Preparation of Sample Solution The preparation of a sample solution shall be in accordance with one of the following methods⁽⁶⁾:

(1) Sample Easy to Be Decomposed by Nitric Acid⁽⁷⁾

- (1.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 20 ml of nitric acid (1 + 1) and decompose by gently heating. Add 15 ml of perchloric acid, and successively heat to generate thick white fume of perchloric acid for 5 to 6 min. After standing to cool, add about 30 ml of warm water and dissolve salts.
- (1.2) Add 2 ml of hydrogen peroxide to this solution. After reducing chromium, decompose excess hydrogen peroxide by boiling and allow to stand to cool. Filter this solution using a filter paper (class 5A)⁽¹⁾ and wash alternately 5 or 6 times by using warm perchloric acid (2 + 100) and warm water. Transfer the filtrate and washings to a 100 ml one mark volumetric flask by washing with water and cool to ordinary temperature. Thereafter, dilute to the mark with water. Discard the residue.

(2) Sample Difficult to Be Decomposed by Nitric Acid⁽⁷⁾ Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of mixed acid and decompose by gently heating. Add 15 ml of perchloric acid, successively heat and generate thick white fume of perchloric acid for 5 to 6 min. After standing to cool, add about 30 ml of warm water and dissolve salts. Hereinafter operate in accordance with the procedure of 4.2.4.1 (1.2).

(3) Sample Containing Vanadium⁽⁸⁾ Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 20 ml of nitric acid (1 + 1) and 15 ml of mixed acid and decompose by gently heating. Add 15 ml of perchloric acid, successively heat and generate thick white fume of perchloric acid for 5 to 6 min. After standing to cool, add about 30 ml of warm water, dissolve salts, add 2 ml of hydrogen peroxide and reduce chromium. Thereafter decompose excess hydrogen peroxide by boiling. After standing to cool, add 5 ml of ammonium iron (II) sulfate solution [4.2.2. (11)] and reduce vanadium. Filter alternately 5 or 6 times by using warm perchloric acid (2 + 100) and warm water. After cooling the filtrate and washings to ordinary temperature, transfer to a 100 ml one-mark volumetric flask by washing with water and dilute to the marked line with water. Discard the residue.

- (4) Sample Containing Tungsten, Niobium, Titanium, Zirconium and Arsenic⁽⁹⁾ Weigh out a sample, transfer to a beaker (200 ml, quartz), cover with a watch glass, add 20 ml of nitric acid (1 + 1) or 15 ml of mixed acid and decompose by gently heating. Add 15 ml of perchloric acid, and successively heat to generate thick white fume of perchloric acid for 5 to 6 min. After standing to cool, add 3 ml of hydrofluoric acid and water and dilute the amount of solution to about 70 ml. Thereafter, dissolve salts by heating. Then, add 3 g of boric acid and sufficiently mix to dissolve. Hereinafter, operate in accordance with the procedure of 4.2.4.1 (1.2).

Notes (6) Use appliances such as a beaker, a one-mark volumetric flask, etc. are preliminarily sufficiently washed with hydrochloric acid (1 + 1) and water.

- (7) This provision shall not be applied to the case where the sample contains tungsten, and the cases where vanadium, niobium, titanium, or zirconium is respectively contained by not less than 0.02 wt% and arsenic is contained by not less than 0.003 wt%.
- (8) This provision applies to the case where a sample contains vanadium by not less than 0.02 wt%. However, this shall not be applied to the case where tungsten is contained and the cases where niobium, titanium, or zirconium is contained respectively by not less than 0.02 wt% and arsenic is contained by not less than 0.003 wt%.
- (9) This provision applies to the cases where tungsten is contained, niobium, titanium, or zirconium is respectively contained by not less than 0.02 wt%, and arsenic is contained by not less than 0.003 wt%.

4.2.4.2 Extracting Separation of Phosphorus The extracting separation of phosphorus shall be in accordance with either of the following methods.

- (1) In the Case Where Acid Concentration Is Regulated with Perchloric Acid Separately take accurately 20 ml of the solution obtained in 4.2.4.1 (1) to (3), transfer to a separating funnel (100 ml), add 8 ml of perchloric acid and water and regulate the amount of solution at 30 ml. Thereafter, sufficiently mix by shaking and allow to stand for about 10 min. Add accurately 20 ml of isobutylacetic acid, vigorously mix by shaking for 1 min and separate into two layers by standing still. Thereafter, discard the lower layer. Add 30 ml of perchloric acid (1 + 3), mix by vigorously shaking for 30 sec and allow to stand still. After separation into two layers, discard the lower layer and filter an organic phase into a vessel with a stopper by using a dry filter paper (class 5A).

- (2) In the Case Where Acid Concentration Is Regulated With Nitric Acid Separately take accurately 10 ml of the sample solution obtained in 4.2.4.1 (4), transfer to a separating funnel (100 ml), add 17 ml of nitric acid, 5 ml of ammonium molybdate solution B [4.2.2 (1)], and water and regulate the amount of solution at 35 ml. Thereafter, mix by sufficiently shaking. After allowing to stand for about 10 min, add accurately 10 ml of isobutylacetic acid, mix by vigorously shaking for 1 min and allow to stand still. After separating into two layers, discard the lower layer. Add 10 ml of nitric acid (1 + 6) mix by vigorously shaking for 1 min, and allow to stand still. After separating into two layers, discard the lower layer and filter the organic layer into a vessel with a stopper by using a dry filter paper (class 5A).

4.2.4.3 Measurement of Absorbance Spray a portion of the organic phase obtained in 4.2.4.2 into a dinitrogen monoxide and acetylene flame of an atomic absorption photometer of which the zero point is regulated by using isobutylacetic acid and measure the absorbance of molybdenum at 313.3 nm in wavelength.

4.2.5 Blank Test Weigh out the same amount of iron as that of the weighed-out sample instead of the sample, and hereinafter operate parallel to the sample in accordance with the procedures of 4.2.4.1 to 4.2.4.3(2).

4.2.6 Preparation of Working Curve The preparation of a working curve⁽¹⁰⁾ shall be as follows:

Prepare seven beakers (300 ml) for each range of phosphorus content, weigh out the same amount of iron [4.2.2.(9)] as the weighed-out amount of a sample given in Table 6, transfer to each thereof, and then add accurately standard phosphorus solution in accordance with Table 7. Hereinafter, operate in accordance with the procedures of 4.2.4.1 to 4.2.4.3(2), prepare the working curve between the absorbance measured parallel to the sample and the amount of phosphorus, parallel transfer the relation curve so as to pass through the origin and take said relation curve as the working curve.

Table 7. Additional Amount of Standard Phosphorus Solution

Phosphorus content wt%	Standard phosphorus solution to be used	Additional amount of standard phosphorus solution ml
0.003 and over, up to 0.005	[4.2.2 (15)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.005 and over, up to 0.010	[4.2.2 (15)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0

Note (10.) A working curve can be prepared by using a standard sample of a known phosphorus content of which the composition is similar to that of a sample. In that case, not less than three kinds of standard samples having different phosphorus contents shall be selected within each phosphorus content range given in Table 6. These standard solutions are operated in accordance with the procedures of 4.2.4.1 to 4.2.4.3. The relation curve between the absorbance measured parallel to the sample and the content of phosphorus is prepared, parallel transferred so as to pass through the origin and said relation curve is taken as the working curve.

The content of phosphorus in the sample in that case is calculated by subtracting the phosphorus content obtained in a blank test from the phosphorus content obtained in sample solution by inserting the absorbances obtained in 4.2.4.3 and 4.2.5 into this working curve.

4.2.7 Calculation Insert the absorbances obtained in 4.2.4.3 and 4.2.5 into the working curve prepared in 4.2.6, obtain respective contents of phosphorus and calculate the content of phosphorus in a sample from the following formula:

$$\text{Phosphorus wt\%} = \frac{A_1 - A_2}{m \times B} \times 100$$

where, A_1 : detection amount of phosphorus in aliquot sample solution (g)
 A_2 : detection amount of phosphorus in aliquot blank test solution⁽¹¹⁾ (g)
 m : weighing out amount of sample (g)
 B : aliquot ratio of sample solution and blank test solution

Note ⁽¹¹⁾ When phosphorus is contained in iron used for a blank test, correct the detection value A_2 by subtracting the amount of phosphorus in the iron weighed out.

4.2.8 Tolerances The tolerances shall be as prescribed in Table 8⁽⁵⁾.

Table 8. Tolerances

Unit: wt%

Phosphorus content	Tolerance in the same laboratory	Tolerance between different laboratories
0.0003 and over, up to 0.010	$D_2 [0.0195 \times (\text{P content}) + 0.00005]$	$D_2 [0.0404 \times (\text{P content}) + 0.00006]$

5. Method for Determination of Nickel

5.1 Determination Method The method for determination of nickel shall be in accordance with acid decomposition direct method. This method applies to the sample 0.003 wt% or over to and excluding 1.0 wt% in nickel content.

5.2 Acid Decomposition Direct Method

5.2.1 Summary After decomposing a sample with suitable acid, the solution is filtered. The filtrate is sprayed into an air and acetylene flame of an atomic absorption photometer and the absorbance thereof is measured.

5.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (2 + 100)
- (2) Perchloric acid

- (3) Aqua regia (three parts by volume of hydrochloric acid and one part by volume of nitric acid)
- (4) Mixed acid (one part by volume of hydrochloric acid, one part by volume of nitric acid, and two parts by volume of water)
- (5) Iron Pure iron as high as possible, which contains no nickel or otherwise of which nickel content is known and as low as possible.
- (6) Standard nickel solution A (500 $\mu\text{g Ni/ml}$) Weigh out 0.500 g of nickel (not less than 99.9 wt%), transfer to a beaker (200 ml), cover with a watch glass, add 30 ml of nitric acid (1 + 1), decompose by gently heating, successively heat, and expel nitrogen oxide or the like. After cooling to ordinary temperature, transfer to a 1000 ml one mark volumetric flask by washing with water, dilute to the marked line with water and take it as the standard nickel solution A.
- (7) Standard nickel solution B (100 $\mu\text{gNi/ml}$) Dilute a fixed amount of standard nickel solution A to accurately five volumes with water and take it as the standard nickel solution B. Prepare this solution at each service.

5.2.3 Weighing out Amount of Sample The weighing out amount of a sample shall be as prescribed in Table 9.

Table 9. Weighing out Amount of Sample

Nickel content wt%	Weighing out amount of sample g
0.003 and over, up to 0.10	1.00
0.10 and over, up to 1.0	0.50

5.2.4 Operation

5.2.4.1 Preparation of Sample Solution The preparation of sample solution shall be in accordance with either of the following methods.

(1) Sample Easy to Be Decomposed by Mixed Acid

- (1.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 20 ml of mixed acid, decompose by heating, and expel nitrogen oxide or the like. Thereafter, allow to stand to cool.
- (1.2) Filter this solution by using a filter paper (class 5A)⁽¹⁾ and wash by using warm hydrochloric acid (2 + 100) and warm water until the yellow of iron (III) chloride is not observed on the filter paper. Transfer the filtrate and washings to a 100 ml one-mark volumetric flask by washing with water, and cool to ordinary temperature. Thereafter, dilute to the marked line with water. Discard the residue.

- (2) Sample Difficult to Be Decomposed by Mixed Acid Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of aqua regia, and decompose by gently heating. Add 15 ml of perchloric acid, successively heat, and generate white fume of perchloric acid for 5 to 6 min. After standing to cool, add about 30 ml of water and dissolve salts. Hereinafter, operate in accordance with the procedure of 5.2.4.1 (1.2).

5.2.4.2 Measurement of Absorbance Spray a portion of solution obtained in 5.2.4.1 into an air and acetylene flame of an atomic absorption photometer of which the zero point is adjusted by using water and measure the absorbance at a wavelength given in Table 10.

Table 10. Wavelength to Be Measured

Nickel content wt%	Wavelength nm
0.003 and over, up to 0.10	232.0
0.10 and over, up to 1.0	352.5

5.2.5 Blank Test Weigh out the same amount of iron [5.2.2 (5)] as that of a weighed-out sample instead of the sample and hereinafter operate parallel to the sample in accordance with the procedures of 5.2.4.1 and 5.2.4.2(2).

5.2.6 Preparation of Working Curve The preparation of a working curve⁽¹²⁾ shall be as follows:

Prepare seven beakers (200 ml) for each range of nickel content, weigh out the same amount of iron [5.2.2 (5)] as the weighing out amount of a sample given in Table 9, transfer to each thereof and then add standard nickel solution accurately in accordance with Table 11. Hereinafter, operate in accordance with the procedures of 5.2.4.1 and 5.2.4.2(2), prepare the relation curve between the absorbance measured parallel to the sample and the amount of nickel, parallel transfer said relation curve so as to pass through the origin and take it as the working curve.

Table 11. Additional Amount of Standard Nickel Solution

Nickel content wt%	Standard nickel solution to be used	Additional amount of standard nickel solution ml
0.003 and over, up to 0.10	B [5.2.2 (7)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.10 and over, up to 1.0	A [5.2.2 (6)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0

Note ⁽¹²⁾ A working curve can be prepared by using standard sample of a known nickel content of which the composition is similar to that of a sample. In that case, not less than three kinds of standard samples having different nickel contents shall be selected from each nickel content range given in Table 9.

These standard samples are operated in accordance with the procedures of 5.2.4.1 and 5.2.4.2 and the relation curve between the absorbance measured parallel to the sample and the content of nickel is prepared. The relation curve is parallel transferred so as to pass through the origin to be taken as the working curve. In that case, the content of nickel in the sample shall be calculated by subtracting the content of nickel obtained in a blank test from the content of nickel obtained in sample solution by inserting the absorbances obtained in 5.2.4.3 and 5.2.5 into this working curve.

5.2.7 Calculation Insert the absorbances obtained in 5.2.4.2 and 5.2.5 into the working curve prepared in 5.2.6, obtain each nickel amount and calculate the content of nickel in a sample from the following formula:

$$\text{Nickel wt\%} = \frac{A_1 - A_2}{m} \times 100$$

where A_1 : detection amount of nickel in sample solution (g)
 A_2 : detection amount of nickel in blank test solution⁽¹³⁾ (g)
 m : weighing out amount of sample (g)

Note ⁽¹³⁾ When nickel is contained in iron used for a blank test, the nickel detection amount is corrected by subtracting the amount of nickel in iron weighed out.

5.2.8 Tolerances The tolerances shall be in accordance with Table 12⁽⁵⁾.

Table 12. Tolerances

Unit: wt%

Nickel content	Tolerance in the same laboratory	Tolerance between different laboratories
0.003 and over, Up to 0.10	$D_2 [0.002 \times (\text{Ni content}) + 0.00036]$	$D_2 [0.0097 \times (\text{Ni content}) + 0.00050]$
0.10 and over, up to 1.0	$D_2 [0.0082 \times (\text{Ni content}) + 0.0019]$	$D_2 [0.0088 \times (\text{Ni content}) + 0.0015]$

6. Method for Determination of Chromium

6.1 Determination Method The method for determination of chromium shall be in accordance with acid decomposition direct method. This method applies to the sample 0.002 wt% or over to and excluding 2.0 wt% in chromium content.

6.2 Acid Decomposition Direct Method

6.2.1 Summary After decomposing a sample by a suitable acid, the solution is filtered. The filtrate is sprayed into a dinitrogen monoxide and acetylene flame of an atomic absorption photometer and the absorbance thereof is measured.

6.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1, 2 + 100)
- (2) Hydrofluoric acid
- (3) Sulfuric acid (1 + 1)
- (4) Aqua regia (three parts by volume of hydrochloric acid and one part by volume of nitric acid)
- (5) Iron Pure iron as high as possible which contains no chromium or otherwise of which chromium content is known and as low as possible.
- (6) Potassium disulfate
- (7) Standard chromium solution A (400 $\mu\text{g Cr/ml}$) Weigh out 1,000 g of chromium (not less than 99.9 wt%), transfer to a beaker (300 ml), cover with a watch glass, add 40 ml of hydrochloric acid (1 + 1) and decompose by gently heating. After cooling to ordinary temperature, transfer to a 1000 ml one-mark volumetric flask by washing with water, dilute to the marked line with water, and take it as the stock solution (1.00 mg Cr/ml). Dilute a fixed amount of this stock solution accurately to 2.5 volumes and take it as the standard chromium solution A. Prepare this solution at each service.
- (8) Standard chromium solution B (100 $\mu\text{g Cr/ml}$) Dilute a fixed amount of stock solution (1.00 mg Cr/ml) to accurately ten volumes with water and take it as the standard chromium solution B. Prepare this solution at each service.

6.2.3 Weighing Out Amount of Sample The weighing out amount of a sample shall be as prescribed in Table 13.

Table 13. Weighing Out Amount of Sample

Chromium content wt%	Weighing out amount of sample g
0.002 and over, up to 0.10	1.00
0.10 and over, up to 2.0	0.20

6.2.4 Operation

6.2.4.1 Preparation of Sample Solution The preparation of sample solution shall be in accordance with either of the following methods:

(1) Sample Easy to Be Decomposed by Aqua Regia

- (1.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of aqua regia, decompose by heating, successively heat, and expel nitrogen oxide or the like. After standing to cool, add about 30 ml of water.

- (1.2) Filter this solution by using a filter paper (class 5A)⁽¹⁾, use warm hydrochloric acid (2 + 100) and warm water, and wash until the yellow of iron (III) chloride is not observed on the filter paper. Transfer the filtrate and washings to a 100 ml one-mark volumetric flask by washing with water, and cool to ordinary temperature. Thereafter, dilute to the marked line with water and discard the residue.

(2) Sample Difficult to Be Decomposed by Aqua Regia

- (2.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of aqua regia, decompose by heating, successively heat, and expel nitrogen oxide or the like. After standing to cool, add about 30 ml of water.
- (2.2) Filter this solution by using a filter paper (class 5B), use warm hydrochloric acid (2 + 100) and warm water, and wash until the yellow of iron (III) chloride is not observed on the filter paper. Reserve the filtrate and washings as main solution.
- (2.3) Transfer insoluble residue together with the filter paper into a platinum crucible (No. 30). After drying, incinerate the filter paper by ignition. After standing to cool, ignite, wet the residue with 2 to 3 drops of sulfuric acid (1 + 1), add 5 ml of hydrofluoric acid and vaporize silicon dioxide and sulfuric acid by gently heating. Add 1 g of potassium disulfate thereto, cover it, at first slowly heat, gradually increase temperature and fuse the residue by heating to dark red heat state. After standing to cool, add 5 ml of hydrochloric acid (1 + 1) and a small amount of warm water to the platinum crucible, dissolve the melt by gently heating and combine it to main solution reserved in (2.2). Wash the platinum crucible with a small amount of water, join washings also to the main solution. Transfer this to a 100 ml one-mark volumetric flask by washing with water and cool to ordinary temperature. Thereafter, dilute to the marked line with water.

6.2.4.2 Measurement of Absorbance Spray a portion of solution obtained in 6.2.4.1 into a dinitrogen monoxide and acetylene flame of an atomic absorption photometer of which the zero point is regulated by using water and measure the absorbance at the wavelength given in Table 14.

Table 14. Measuring Wavelength

Chromium content wt%	Wavelength nm
0.002 and over, up to 0.50	357.9
0.50 and over, up to 2.0	425.4

6.2.5 Blank Test Weigh out the same amount of iron [6.2.2 (5)] as that of a weighed-out sample instead of the sample and operate parallel to the sample in accordance with the procedures of 6.2.4.1 to 6.2.4.2⁽²⁾.

6.2.6 Preparation of Working Curve The preparation of a working curve⁽¹⁴⁾ shall be as follows:

Prepare seven beakers (200 ml) for each range of chromium content, transfer the same amount of iron [6.2.2 (5)] as that of the weighed-out amount of a sample given in Table 13 to each of them, and then add accurately standard chromium solution in accordance with Table 15. Hereinafter, operate in accordance with the procedures of 6.2.4.1 to 6.2.4.2(2), prepare the relation curve between the absorbance measured parallel to the sample and the amount of chromium, parallel transfer the relation curve so as to pass through the origin and take it as the working curve.

Table 15. Additional Amount of Standard Chromium Solution

Chromium content wt%	Standard chromium solution to be used	Additional amount of standard chromium solution ml
0.002 and over, up to 0.10	B [6.2.2 (8)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.10 and over, up to 0.50	B [6.2.2 (8)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.50 and over, up to 2.0	A [6.2.2 (7)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0

Note ⁽¹⁴⁾ A working curve can be prepared by using a standard sample of a known chromium content of which the composition is similar to that of a sample. In that case, not less than three kinds of standard samples having different chromium contents shall be selected from each chromium content range given in Table 13. Operate these standard samples in accordance with the procedures of 6.2.4.1 and 6.2.4.2, prepare the relation curve between the absorbance measured parallel to the sample and the amount of chromium, parallel transfer the relation curve so as to pass through the origin and take it as the working curve. In that case, the content of chromium in the sample shall be calculated by subtracting the content of chromium obtained in a blank test from the content of chromium obtained in sample solution by inserting the absorbances obtained in 6.2.4.2 and 6.2.5 into this working curve.

6.2.7 Calculation Insert the absorbances obtained in 6.2.4.2 and 6.2.5 into the working curve prepared in 6.2.6, obtain each amount of chromium and calculate the content of chromium in a sample from the following formula:

$$\text{Chromium wt\%} = \frac{A_1 - A_2}{m} \times 100$$

where

A_1 : detection amount of chromium in sample solution (g)

A_2 : detection amount of chromium in blank test solution⁽¹⁵⁾ (g)

m : weighing out amount of sample (g)

Note (15) When some chromium is contained in iron used for a blank test, the detection amount of chromium is corrected by subtracting the amount of chromium in the weighed-out iron.

6.2.8 Tolerances The tolerances shall be in accordance with Table 16(5).

Table 16. Tolerances

Unit: wt%

Chromium content wt%	Tolerance in the same laboratory	Tolerance in different laboratories
0.002 and over, up to 0.50	$D_2 [0.0118 \times (\text{Cr content}) + 0.00015]$	$D_2 [0.0177 \times (\text{Cr content}) - 0.00006]$
0.50 and over, up to 2.0	$D_2 [0.0025 \times (\text{Cr content}) + 0.0053]$	$D_2 [0.0079 \times (\text{Cr content}) + 0.0027]$

7. Method for Determination of Molybdenum

7.1 Determination Method The method for determination of molybdenum shall be in accordance with acid decomposition direct method. This method applies to the sample 0.01 wt% or over to and excluding 1.0 wt% in molybdenum content.

7.2 Acid Decomposition Direct Method

7.2.1 Summary After decomposing a sample by suitable acid, filter the solution. After adding aluminium chloride to this solution, spray it into a di-nitrogen monoxide and acetylene flame of an atomic absorption photometer and measure the absorbance thereof.

7.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1, 2 + 100)
- (2) Nitric acid
- (3) Perchloric acid
- (4) Aqua regia (three parts by volume of hydrochloric acid and one part by volume of nitric acid)
- (5) Mixed acid A (one part by volume of hydrochloric acid, one part by volume of nitric acid, and two parts by volume of water)
- (6) Mixed acid B (three parts by volume of hydrochloric acid, three parts by volume of phosphoric acid, and 16 parts by volume of water)
- (7) Iron Pure iron as high as possible which has no molybdenum or otherwise of which molybdenum content is known and as low as possible.

- (8) Aluminium solution (12 mg Al/ml) Dissolve 110 g of aluminium chloride hexahydrate in water and dilute the amount of solution to 1 l.
- (9) Standard molybdenum solution (500 µg Mo/ml) Weigh out 0.500 g of molybdenum (not less than 99.9 wt%), transfer to a beaker (200 ml), cover with a watch glass, add 30 ml of hydrochloric acid (1 + 1) and a small amount of nitric acid, decompose by gently heating, successively heat, and expel nitrogen oxide or the like. After cooling to ordinary temperature, transfer to a 1000 ml one-mark volumetric flask by washing with water, dilute to the marked line with water and take it as the standard molybdenum solution.

7.2.3 Weighing Out Amount of Sample The weighing out amount of a sample shall be in accordance with Table 17.

Table 17. Weighing out Amount of Sample

Molybdenum content wt%	Weighing out amount of sample g
0.01 and over, up to 0.50	1.00
0.50 and over, up to 1.0	0.50

7.2.4 Operation

7.2.4.1 Preparation of Sample Solution The preparation of sample solution shall be in accordance with one of the following methods⁽¹⁶⁾.

(1) Sample Easy to Be Decomposed by Mixed Acid A⁽¹⁷⁾

- (1.1) Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 20 ml of mixed acid A, decompose by heating, successively heat, and expel nitrogen oxide or the like. Add 20 ml of hydrochloric acid (1 + 1) and heat. After dissolving salts, allow to stand to cool.
- (1.2) Filter this solution by using a filter paper (class 5A)⁽¹⁾, use warm hydrochloric acid (2 + 100) and warm water, and wash until the yellow of iron (III) chloride is not observed on the filter paper. Transfer the filtrate and washings to a 100 ml one-mark volumetric flask by washing with water, add accurately 10 ml of aluminium solution [7.2.2 (8)] and cool to ordinary temperature. Thereafter, dilute to the marked line with water. Discard the residue.

- (2) Sample Difficult to Be Decomposed by Mixed Acid A⁽¹⁷⁾ Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, add 15 ml of aqua regia, and decompose by gently heating. Add 15 ml of perchloric acid, successively heat, and generate white fume of perchloric acid for 5 to 6 min. After standing to cool, add 30 ml of water, and dissolve salts. Hereinafter, operate in accordance with the procedure of 7.2.4.1 (1.2).

- (3) Sample Containing Tungsten Weigh out a sample, transfer to a beaker (200 ml), cover with a watch glass, and add 30 ml of mixed acid B. After decomposition by heating, add 3 ml of nitric acid, and oxidize iron or the like by heating. Successively heat, and generate thick white fume of sulfuric acid. After standing to cool, add about 30 ml of water, and heat until salts are dissolved. Hereinafter, operate in accordance with the procedure of 7.2.4.1 (1.2).

Notes (16) Since molybdenum is occasionally difficult to be decomposed because of formation of carbide or the like, it is required to select suitable acid for decomposition.

- (17) This provision shall not be applied to the case where tungsten is contained in the sample.

7.2.4.2 Measurement of Absorbance Spray a portion of solution obtained in 7.2.4.1 into a dinitrogen monoxide and acetylene flame of an atomic absorption photometer of which the zero point is adjusted by using water and measure the absorbance at 313.3 nm in wavelength.

7.2.5 Blank Test Weigh out the same amount of iron [7.2.2 (7)] as the weighed-out amount of a sample instead of the sample and operate parallel to the sample in accordance with the procedures of 7.2.4.1 to 7.2.4.2(2).

7.2.6 Preparation of Working Curve The preparation of a working curve⁽¹⁸⁾ shall be as follows:

Prepare seven beakers (200 ml) for each range of molybdenum content, weigh out the same amount of iron [7.2.2 (7)] as the weighing out amount of a sample given in Table 17, transfer to each of them, and then add accurately standard molybdenum solution in accordance with Table 18. Hereinafter, operate in accordance with the procedures of 7.2.4.1 to 7.2.4.2(2), prepare the relation curve between the absorbance measured parallel to the sample and the amount of molybdenum, parallel transfer the relation curve so as to pass the origin and take it as the working curve.

Table 18. Additional Amount of Standard Molybdenum Solution

Molybdenum content wt%	Standard molybdenum solution to be used	Additional amount of standard molybdenum solution ml
0.01 and over, up to 0.50	[7.2.2 (9)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0
0.50 and over, up to 1.0	[7.2.2 (9)]	0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0

Note (18) A working curve can be prepared by using standard sample of a known molybdenum content of which the composition is similar to that of a sample. In that case, not less than three kinds of standard samples having different molybdenum contents shall be selected within each molybdenum content range given in Table 17. These standard samples are operated in accordance with the procedures of 7.2.4.1 to 7.2.4.2, and the relation curve between the absorbance measured parallel to the sample and the content of molybdenum is prepared. The relation curve is parallel transferred so as to pass through the origin and taken as the working curve. In that case, the content of molybdenum in the sample shall be calculated by subtracting the content of molybdenum obtained in a blank test from the content of molybdenum obtained in sample solution by inserting the absorbances obtained in 7.2.4.2 and 7.2.5 into this working curve.

7.2.7 Calculation Insert the absorbance obtained in 7.2.4.2 and 7.2.5 into the working curve prepared in 7.2.6, obtain each molybdenum amount, and calculate the content of molybdenum in a sample from the following formula:

$$\text{Molybdenum wt\%} = \frac{A_1 - A_2}{m} \times 100$$

where A_1 : detection amount of molybdenum in sample solution (g)
 A_2 : detection amount of molybdenum in blank test solution (19) (g)
 m : weighing out amount of sample (g)

Note (19) When molybdenum is contained in iron used for a blank test, the detection amount of molybdenum herein is corrected by subtracting the amount of molybdenum in the weighed-out iron.

7.2.8 Tolerances The tolerances shall be as prescribed in Table 19(5).

Table 19. Tolerances

Unit: wt%

Molybdenum content	Tolerance in the same laboratory	Tolerance between different laboratories
0.01 and over, up to 1.0	$D_2 [0.0124 \times (\text{Mo content}) + 0.0016]$	$D_2 [0.0180 \times (\text{Mo content}) + 0.0019]$

8. Method for Determination of Copper

8.1 Determination Method The method for determination of copper shall be in accordance with acid decomposition direct method. This method applies to the sample 0.003 wt% or over to and excluding 1.0 wt%.

8.2 Acid Decomposition Direct Method

8.2.1 Summary After decomposing a sample by suitable acid, the solution is filtered. The filtrate is sprayed into an air and acetylene flame of an atomic absorption photometer and the absorbance thereof is measured.