

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for chemical analysis
of gallium arsenide**

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JAPANESE INDUSTRIAL STANDARD

J I S

Methods for chemical analysis of
gallium arsenide

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1. Scope

This Japanese Industrial Standard specifies the determination method of chromium, copper, iron, manganese, silicon, boron, zinc, indium, and tellurium in gallium arsenide crystal.

Remarks: Applicable Standards to this Standard are shown in the following:

JIS K 0050 General Rules for Chemical Analysis

JIS K 0116 General Rules for Emission Spectrochemical Analysis

JIS K 0121 General Rules for Atomic Absorption Spectrochemical Analysis

JIS K 8005 Standard Substances for Volumetric Analysis

JIS Z 8401 Rules for Rounding off of Numerical Values

2. General matters

General matters common in this Standard shall be as follows:

- (1) General matters common to methods for chemical analysis are in accordance with JIS K 0050, JIS K 0116 and JIS K 0121.
- (2) Perform the analysis operation, as a rule, in a clean room.
- (3) High-purity water The water (JIS K 0050) refined by distillation twice by using a distillation apparatus made of quartz or the refined water equivalent or superior thereto. For preservation, quartz vessel or ethylene tetrafluoride resin (hereafter referred to as the "PTFE") vessel is used.
- (4) Apparatus
 - (a) Beaker and test tube Use the beaker and test tube made of quartz or PTFE. After immersing these apparatus into warm nitric acid for not less than one day before using, preserve in nitric acid (1 + 1000). At each using, wash sufficiently with high purity water and dry to use.
 - (b) Preservation vessel Use the preservation vessel made of quartz, PTFE or polyethylene. Prior to using, after immersing these vessels into warm nitric acid for one day or more, preserve in nitric acid (1 + 1000). At each time of use, wash sufficiently with high purity water and dry to use.

3. Taking and dealing methods of sample

3.1 Taking method of sample The taking method of sample shall be as follows:

- (1) Cut out from the ingot or block of gallium arsenide crystal to the suitable thickness and width by using a diamond cutter or the like.
- (2) Cut the cut out sample to about 0.1 to 0.2 g in weight and take it as the sample for chemical analysis.
- (3) In case where the taking method of sample for chemical analysis is impossible to be in accordance with the specifications of (1) and (2), it is to be in accordance with agreement between the parties concerned with delivery.

3.2 Dealing of sample The dealing of sample shall be as follows:

- (1) As to the sample for analysis, after removing by washing sufficiently the oils and the like on the surface preliminarily with acetone or the like, air-dry.
- (2) In order to prevent staining by foreign matter or the like put the sample for chemical analysis into a polyethylene vessel attached with a suitable lid or the like, and tightly stopper to preserve.
- (3) Take the sample for analysis prior to analysis into a quartz beaker or PTFE beaker, by using the solution mixed with sulphuric acid 3, hydrogen peroxide 1 and water 1 heat for about 5 min to remove the stain on the surface, thereafter wash with high purity water, and acetone in sequence, and air-dry.

3.3 Weighing method of sample The weighing method of sample shall be as follows:

- (1) At the time of weighing out of sample for chemical analysis, with taking care sufficiently to the surface stain of sample, weigh out by using a clean polyethylene or PTFE pincette.
- (2) For weighing and of sample for chemical analysis, as a rule, use a chemical balance and read out to the nearest 1 mg.

4. Arrangement of analysis value

4.1 Number of times of analysis As a rule, carry out the analysis repeatedly twice in the same analysis place.

4.2 Blank test At the time of analysis, carry out the blank test and correct the measured value.

4.3 Indicating of analysis value Express the analysis value by mass percentage, in the case of less than 0.0001 wt % round off to six places of decimals and in the case of not less than 0.0001 wt % round off to three significant figures according to JIS Z 8401.

Further, in the case where atom number per 1 cm³ (atoms/cm³) of analysis value is required to be expressed, convert from the mass percentage according to the following formula.

$$A = \frac{3.02 \times 10^{18}}{M} \times B \times 10^4$$

where, A : atom number (atoms/cm³) of objective element per 1 cm³ of gallium arsenide crystal.

B : mass percentage of objective element (wt %)

M : atomic weight of objective element

5. Chromium determination methods

5.1 Division of determination methods The determination method of chromium shall be in accordance with either of the following.

- (1) Flameless atomic absorption spectrometry (Carbon furnace) This method applies to the sample not less than 0.00002 wt % in chromium content and not more than 0.0010 wt %.
- (2) Flameless atomic absorption spectrometry (Tungsten furnace) This method applies to the sample not less than 0.00002 wt % in chromium content and not more than 0.0010 wt %.
- (3) Inductively coupled plasma emission spectroscopy This method applies to the sample not less than 0.00002 wt % in chromium content and not more than 0.0010 wt %.

5.2 Flameless atomic absorption spectrometry (Carbon furnace)

5.2.1 Summary After decomposing the sample with hydrochloric acid and nitric acid, pour the solution into carbon furnace of flameless atomic absorption photometer and heat, then measure the absorbance.

5.2.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) Mix hydrochloric acid 1 and water 1, and refine according to non-boiling distillation with a quartz distilling apparatus. For preservation, use a PTFE vessel.
- (2) Nitric acid Refine the nitric acid according to non-boiling distillation with a quartz distilling apparatus. For preservation use a PTFE vessel.
- (3) Gallium (99.9999 wt % min.)
- (4) Arsenic (99.9999 wt % min.)
- (5) Gallium arsenide The gallium arsenide crystal containing almost no chromium. By using the mixed solution of sulphuric acid 3, hydrogen peroxide 1, and water 1, heat this gallium arsenide crystal for about 5 min to remove the stains on the surface, thereafter wash sequentially with high purity water, acetone, air-dry and preserve in a polyethylen vessel.

- (6) Standard chromium solution A ($2 \mu\text{g Cr/ml}$) Dissolve potassium dichromate (JIS K 8005) 0.283 g in water approx. 100 ml, transfer by using water to 1000 ml one mark volumetric flask, dilute with water up to the marked line take it as the stock solution ($100 \mu\text{g Cr/ml}$), or decompose by heating the chromium (99.9 wt % min.) 0.100 g by hydrochloric acid (1 + 1) 200 ml, after cooling to ordinary temperature, transfer by using water to 1000 ml one mark volumetric flask, dilute with water up to the marked line and take it as the stock solution ($100 \mu\text{g Cr/ml}$). Transfer this stock solution to a polyethylene bottle and preserve it. At each time of use of this stock solution, dilute the required amount with water correctly 50 times and take it as the standard chromium solution A.
- (7) Standard chromium solution B ($0.3 \mu\text{g Cr/ml}$) Take out the standard chromium solution A ($2 \mu\text{g Cr/ml}$) of (6) 15.0 ml into a 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard chromium solution B. Prepare this solution at each time of use.
- (8) Standard chromium solution C ($0.2 \mu\text{g Cr/ml}$) Take out 10.0 ml of standard chromium solution A ($2 \mu\text{g Cr/ml}$) of (6) into a 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard chromium solution C. Prepare this solution at each time of use.
- (9) Standard chromium solution D ($0.04 \mu\text{g Cr/ml}$) Take out 20.0 ml of standard chromium solution C ($0.2 \mu\text{g Cr/ml}$) of (8) into a 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard chromium solution D. Prepare this solution at each time of use.

5.2.3 Weighing-out amount of sample The weighing-out amount of sample shall be as given in Table 1.

Table 1. Weighing-out amount of sample

Chromium content rate wt %	Weighing-out amount of sample g
0.00002 or over to and excl. 0.0003	0.20
0.0003 or over up to and incl. 0.0010	0.10

5.2.4 Operation

5.2.4.1 Preparation of sample solution The preparation of sample solution shall be carried out according to the following procedures:

- (1) Weigh out the sample, transfer to a test tube (¹).

- (2) Add hydrochloric acid (1 + 1) [5.2.2 (1)] about 3 ml, gently shake to mix, and after discarding the solution, wash several times with about 5 ml of high-purity water ⁽²⁾.
- (3) Add hydrochloric acid (1 + 1) [5.2.2 (1)] 5 ml and nitric acid [5.2.2 (2)] 2.5 ml, heat at 50 to 70°C to dissolve and thereafter successively continue heating to concentrate until the liquid amount becomes about 5 ml.
- (4) After cooling to ordinary temperature, dilute with high-purity water up to the carved mark ⁽³⁾.

Notes ⁽¹⁾ Use the test tube having carved marks of 10 ml and 20 ml.

⁽²⁾ In this operation, disregard the dissolution amount of sample.

⁽³⁾ In the case where the weighing-out amount of sample is 0.20 g dilute up to the carved mark of 10 ml, and in the case of 0.10 g, up to the carved mark of 20 ml.

5.2.4.2 Measuring of absorbance Pour a definite amount ⁽⁴⁾ of solution obtained in 5.2.4.1 (4) into a carbon furnace of flameless atomic absorption photometer, heat and measure the absorbance at a wavelength of 357.9 nm.

Note ⁽⁴⁾ Generally, 10 µl or 20 µl is poured-in, but the pouring-in amount is determined by matching with the measuring range of the using apparatus.

5.2.5 Blank test Take the absorbance of solution not added with standard chromium solution obtained in the working curve preparing operation of 5.2.6 as the absorbance of blank test.

5.2.6 Preparing of working curve The preparing of working curve shall be in accordance with either one of the following.

(1) The case of using gallium and arsenic

- (a) Weigh out several pieces of gallium [5.2.2 (3)] of half amount of sample weighing amount and the arsenic [5.2.2 (4)] of the half amount and transfer to respective test tubes ⁽¹⁾.
- (b) After performing the operation of 5.2.4.1 (3), cool to ordinary temperature.
- (c) In the case where the weighing-out amount of sample is 0.20 g, add stepwise the standard chromium solution D [5.2.2 (9)] 0 to 4.0 ml and standard chromium solution C [5.2.2 (8)] 1.0 to 3.0 ml (as chromium 0 to 0.60 µg) and dilute with high-purity water up to the carved mark of 10 ml.

In the case where the weighing-out amount of sample is 0.10 g, add stepwise the standard chromium solution B [5.2.2 (7)] 0 to 4.0 ml (as chromium 0 to 1.2 µg), and dilute with high-purity water up to the carved mark of 20 ml.

- (d) Pour a definite amount ⁽⁵⁾ of this solution into the carbon furnace of flameless atomic absorption photometer, heat, measure the absorbance at wavelength of 357.9 nm in parallel to sample, prepare the relation curve of the obtained absorbance and the chromium amount, transfer the relation curve in parallel so as to pass the origin and take it as the working curve.

Note ⁽⁵⁾ Make the same amount as the pouring amount used in 5.2.4.2.

(2) Case where gallium arsenide is used

- (a) Weigh out several pieces of gallium arsenide [5.2.2 (5)] of the same amount as the weighing-out amount of sample, and after transferring respectively to test tubes ⁽¹⁾, carry out the operation of 5.2.4.1 (2).
- (b) Operate according to the procedures of (b) to (d) of 5.2.6 (1).

5.2.7 Calculation Obtain the chromium amount from the absorbance obtained in 5.2.4.2 and 5.2.5 and the working curve prepared in 5.2.6 and calculate the chromium content rate according to the following formula.

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

where, A_1 : chromium detected amount in sample solution (g)

A_2 : chromium detected amount in blank test solution (g)

m : weighing-out amount of sample (g)

5.3 Flameless atomic absorption spectrometry (Tungsten furnace)

5.3.1 Summary After decomposing the sample with hydrochloric acid and bromine, add ammonium chloride. Pour this solution into tungsten furnace of flameless atomic absorption photometer to heat and measure the absorbance.

5.3.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) The hydrochloric acid (1 + 1) is in accordance with 5.2.2 (1).
- (2) Bromine
- (3) Ammonium chloride solution (100 g/l) Take hydrochloric acid (1 + 1) [5.3.2 (1)] 65 ml into a quartz beaker (200 ml) or PTFE beaker (200 ml), after adding aqueous ammonia 25 ml while mixing by stirring; leave cool and make the liquid amount 100 ml with high-purity water.
- (4) Gallium (99.9999 wt % min.)
- (5) Arsenic (99.9999 wt % min.)

- (6) Gallium arsenide The gallium arsenide is in accordance with 5.2.2 (5).
- (7) Standard chromium solution A ($2 \mu\text{gCr/ml}$) The standard chromium solution A ($2 \mu\text{gCr/ml}$) is in accordance with 5.2.2 (6).
- (8) Standard chromium solution B ($0.3 \mu\text{gCr/ml}$) The standard chromium solution B ($0.3 \mu\text{gCr/ml}$) is in accordance with 5.2.2 (7).
- (9) Standard chromium solution C ($0.2 \mu\text{gCr/ml}$) The standard chromium solution ($0.2 \mu\text{gCr/ml}$) is in accordance with 5.2.2 (8).
- (10) Standard chromium solution D ($0.04 \mu\text{gCr/ml}$) The standard chromium solution D ($0.04 \mu\text{gCr/ml}$) is in accordance with 5.2.2 (9).

5.3.3 Weighing-out amount of sample The weighing-out amount of sample shall be in accordance with Table 1 of 5.2.3.

5.3.4 Operation

5.3.4.1 Preparation of sample solution The preparation of sample solution shall be performed according to the following procedures:

- (1) Weigh out the sample and transfer to a test tube ⁽¹⁾.
- (2) Add hydrochloric acid (1 + 1) [5.3.2 (1)] about 3 ml, mix by shaking gently and after discarding the solution, wash with high-purity water about 5 ml several times ⁽²⁾.
- (3) After adding hydrochloric acid (1 + 1) [5.3.2 (1)] 2 ml, add little by little the bromine 1 ml to decompose and leave cool.
- (4) Ammonium chloride solution [5.3.2 (3)] 2.5 ml.
- (5) After cooling to ordinary temperature, dilute with high-purity water up to the carved mark ⁽³⁾.

Remarks: As to Notes ⁽¹⁾ to ⁽³⁾, refer to Notes of 5.2.4.1.

5.3.4.2 Measurement of absorbance Pour a definite amount ⁽⁴⁾ of solution obtained in 5.3.4.1 (5) into the tungsten furnace of flameless atomic absorption photometer, heat, and measure the absorbance at wavelength of 357.9 nm.

Remarks: As to Note ⁽⁴⁾ refer to Note of 5.2.4.2.

5.3.5 Blank test The absorbance of solution not added with standard chromium solution to be obtained in working curve preparing operation of 5.3.6 shall be taken as the absorbance of the blank test.

5.3.6 Preparation of working curve The preparation of a working curve shall be in accordance with either one of the following:

(1) Case where gallium and arsenic are used

- (a) Weigh out the gallium [5.3.2 (4)] of half amount of weighing-out amount of sample and arsenic [5.3.2 (5)] of the half amount in several pieces, and transfer to respective test tubes ⁽¹⁾.
- (b) After performing the operation of 5.3.4.1 (3) to (4), cool to ordinary temperature.
- (c) In the case where the weighing-out amount of sample is 0.20 g, add stepwise the standard chromium solution D [5.3.2 (10)] 0 to 4.0 ml and standard chromium solution C [5.3.2 (9)] 1.0 to 3.0 ml (as chromium 0 to 0.60 µg), and dilute with high-purity water up to the carved mark of 10 ml.

In the case where the weighing-out amount of sample is 0.10 g, add stepwise the standard chromium solution B [5.3.2 (8)] 0 to 4.0 ml (as chromium 0 to 1.2 µg), and dilute up to the carved mark of 20 ml.

- (d) Pour a definite amount ⁽⁶⁾ of this solution into the tungsten furnace of flameless atomic absorption photometer to heat, measure the absorbance at wavelength 357.9 nm in parallel to sample, prepare the relation curve between the obtained absorbance and the chromium amount, transfer in parallel the relation curve so as to pass the origin and take it as the working curve.

Note ⁽⁶⁾ Make the same amount as the pouring amount used in 5.3.4.2.

(2) Case where gallium arsenide is used

- (a) Weigh out gallium arsenide [5.3.2 (6)] of the same amount as the sample weighing-out amount in several pieces, after transferring to respective test tubes ⁽¹⁾, carry out the operation of 5.3.4.1 (2).
- (b) Operate according to the procedures of (b) to (d) of 5.3.6 (1).

5.3.7 Calculation Obtain the chromium amount from the absorbances obtained in 5.3.4.2 and 5.3.5 and the working curve prepared in 5.3.6 and calculate the chromium content rate in the sample according to the following formula.

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

where, A_1 : chromium detection amount in sample solution (g)

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

m : weighing-out amount of sample (g)

5.4 Inductively coupled plasma emission spectroscopy

5.4.1 Summary After decomposing the sample with hydrochloric acid and nitric acid, spray the solution into argon plasma of inductively coupled plasma emission spectrochemical apparatus, and measure the emission density.

5.4.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) The hydrochloric acid (1 + 1) is in accordance with 5.2.2 (1).
- (2) Nitric acid The nitric acid is in accordance with 5.2.2 (2).
- (3) Gallium (99.9999 wt % min.)
- (4) Arsenic (99.9999 wt % min.)
- (5) Gallium arsenide The gallium arsenide is in accordance with 5.2.2 (5).
- (6) Standard chromium solution A (2 µgCr/ml) The standard chromium solution A is in accordance with 5.2.2 (6).
- (7) Standard chromium solution B (0.3 µgCr/ml) The standard chromium solution B is in accordance with 5.2.2 (7).
- (8) Standard chromium solution C (0.1 µgCr/ml) Take out the standard chromium solution A (2 µgCr/ml) 5.0 ml of (6) into a one mark volumetric flask of 100 ml, dilute with water up to the marked line and take it as the standard chromium solution C. Prepare this solution at each time of using.

5.4.3 Weighing-out amount of sample The weighing-out amount of sample shall be 0.50 g.

5.4.4 Operation

5.4.4.1 Preparation of sample solution The preparation of sample solution shall be carried out according to the following procedures:

- (1) Weigh out the sample, transfer to test tube (7).
- (2) Add hydrochloric acid (1 + 1) [5.4.2 (1)] about 3 ml, mix by shaking gently, and after discarding the solution, wash by using high-purity water about 5 ml several times (2).
- (3) Add hydrochloric acid (1 + 1) [5.4.2 (1)] 5 ml and nitric acid [5.4.2 (2)] 2.5 ml, after decomposing by heating at 50 to 70°C, successively continue heating and concentrate until the liquid amount becomes about 5 ml.
- (4) After cooling to ordinary temperature, dilute with high-purity water up to the carved mark.

Note (7) Use the test tube having carved mark of 10 ml.

Remarks: As to Note (2), refer to Note of 5.2.4.1.

5.4.4.2 Measurement of emission intensity Spray a part of solution obtained in 5.4.4.1 (4) into argon plasma of inductively coupled plasma emission spectrochemical apparatus, and measure the emission intensity at wavelength of 267.716 nm ⁽⁸⁾.

Note ⁽⁸⁾ If the accuracy and correctness are confirmed, it may be measured by using other wavelength, and in an apparatus capable of measuring the higher order spectral line, it may be used higher order spectral line.

Further, in the apparatus attached with the background correcting mechanism, the background correcting mechanism may be used.

5.4.5 Blank test The emission density of solution without adding of standard chromium solution to be obtained in working curve preparing operation of 5.4.6 shall be taken as the blank test emission density.

5.4.6 Preparing of working curve The preparing of working curve shall be in accordance with either one of the following:

(1) In the case of using gallium and arsenic

- (a) Weigh out the gallium [5.4.2 (3)] of half amount of weighing-out amount of sample and the arsenic [5.4.2 (4)] of half amount by several pieces and transfer respectively into test tubes ⁽⁷⁾.
- (b) After performing the operation of 5.4.4.1 (3), cool to ordinary temperature.
- (c) Add stepwise the standard chromium solution C [5.4.2 (8)] 0 to 4.0 ml, standard chromium solution B [5.4.2 (7)] 2.0 to 4.0 ml and standard chromium solution A [5.4.2 (6)] 1.0 to 3.0 ml (as chromium, 0 to 6.0 µg), and dilute with high-purity water up to the carved mark of 10 ml.
- (d) Spray a part of this solution into argon plasma of inductively coupled plasma emission spectrochemical apparatus, measure the emission density at wavelength 267.716 nm in parallel to the sample ⁽⁸⁾, prepare the relation curve of the obtained emission density and the chromium amount, transfer in parallel the relation curve so as to pass the origin and take it as the working curve.

(2) In the case of using gallium arsenide

- (a) Weigh out the gallium arsenide [5.4.2 (5)] of the same amount as the weighing-out amount of sample in several pieces, and after transferring respectively into test tubes ⁽⁷⁾, carry out the operation of 5.4.4.1 (2).
- (b) Operate according to the procedures of (b) to (d) of 5.4.6 (1).

5.4.7 Calculation Obtain the chromium amount from the emission density obtained in 5.4.4.2 and 5.4.5 and the working curve prepared in 5.4.6, and calculate the chromium content rate in the sample according to the following formula.

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

where, A_1 : chromium detecting amount in sample solution (g)
 A_2 : chromium detecting amount in blank test solution (g)
 m : weighing-out amount of sample (g)

6. Copper determination methods

6.1 Division of determination methods The determination of copper shall be in accordance with either one of the following.

- (1) Flameless atomic absorption spectrometry (Carbon furnace) This method applies to the sample not less than 0.00005 wt % and not more than 0.0010 wt % in copper content rate.
- (2) Flameless atomic absorption spectrometry (Tungsten furnace) This method applies to the sample of copper content rate not less than 0.00005 wt % and not more than 0.0010 wt %.
- (3) Inductively coupled plasma emission spectroscopy This method applies to the sample of copper content rate not less than 0.00005 wt % and not more than 0.0010 wt %.

6.2 Flameless atomic absorption spectrometry (Carbon furnace)

6.2.1 Summary After decomposing the sample with hydrochloric acid and nitric acid, pour the solution into the carbon furnace of flameless atomic absorption photometer to heat and measure the absorbance.

6.2.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) The hydrochloric acid (1 + 1) is in accordance with 5.2.2 (1).
- (2) Nitric acid The nitric acid is in accordance with 5.2.2 (2).
- (3) Gallium (99.9999 wt % min.)
- (4) Arsenic (99.9999 wt % min.)
- (5) Gallium arsenide The gallium arsenide crystal containing almost no copper. Heat this gallium arsenide crystal for about 5 min by using the solution mixed with sulphuric acid 3, hydrogen peroxide 1 and water 1 to remove the stains on the surface, thereafter wash sequentially with high-purity water and acetone, and air-dry to preserve in a polyethylene vessel.

- (6) Standard copper solution A ($2 \mu\text{gCu/ml}$) Decompose copper (99.9 wt % min.) not less than 0.100 g by water 10 ml and nitric acid 3 ml, after cooling to ordinary temperature, transfer to 1000 ml one mark volumetric flask by using water, dilute with water up to the marked line and take it as the stock solution ($100 \mu\text{gCu/ml}$). Transfer this stock solution to polyethylene bottle and preserve it. At each time of use, dilute this stock solution of required amount with water correctly to 50 times and take it as the standard copper solution A.
- (7) Standard copper solution B ($0.3 \mu\text{gCu/ml}$) Take the standard copper solution A ($2 \mu\text{gCu/ml}$) 15.0 ml of (6) into 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard copper solution B. Prepare this solution at each using.
- (8) Standard copper solution C ($0.2 \mu\text{gCu/ml}$) Take standard copper solution A of (6) ($2 \mu\text{gCu/ml}$) 10.0 ml into 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard copper solution C. Prepare this solution at each use.
- (9) Standard copper solution D ($0.05 \mu\text{gCu/ml}$) Take copper standard solution C of (8) ($0.2 \mu\text{gCu/ml}$) 25.0 ml into 100 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard copper solution D. Prepare this solution at each use.

6.2.3 Weighing -out amount of sample The weighing-out amount of sample shall be as given in Table 2.

Table 2. Weighing-out amount of sample

Copper content rate wt %	Weighing-out amount of sample g
0.00005 or over to and excl. 0.0003	0.20
0.0003 or over up to and incl. 0.0010	0.10

6.2.4 Operation

6.2.4.1 Preparation of sample solution Prepare the sample solution according to 5.2.4.1.

6.2.4.2 Measuring of absorbance Pour a definite amount (⁴) of solution obtained in 6.2.4.1 into the carbon furnace of a flameless atomic absorption photometer, heat, and measure the absorbance at wavelength 324.8 nm.

Remarks: As to Note (⁴) refer to Note of 5.2.4.2.

6.2.5 Blank test The absorbance of solution without adding of standard copper solution to be obtained in working curve preparing operation of 6.2.6 shall be taken as the absorbance of blank test.

6.2.6 Preparation of working curve The preparation of a working curve shall be in accordance with either one of the following:

(1) In the case of using gallium and arsenic

- (a) Weigh out the gallium [6.2.2 (3)] of half amount of sample weighing-out amount and the arsenic [6.2.2 (4)] of the half amount in several pieces and transfer respectively into test tubes ⁽¹⁾.
- (b) After performing the operating of 5.2.4.1 (3), cool to ordinary temperature.
- (c) In the case where the weighing-out amount of sample is 0.20 g, add stepwise the standard copper solution D [6.2.2 (9)] 0 to 3.0 ml and standard copper solution C [6.2.2 (8)] 1.0 to 3.0 ml (as copper 0 to 0.60 µg), and dilute with high-purity water up to the carved mark of 10 ml.

In the case where the weighing-out amount of sample is 0.10 g, add stepwise standard copper solution B [6.2.2 (7)] 0 to 4.0 ml (as copper 0 to 1.2 µg) and dilute with high-purity water up to the carved mark of 20 ml.

- (d) Pour a definite amount ⁽⁹⁾ of this solution into the carbon furnace of flameless atomic absorption photometer, heat, measure the absorbance at wavelength 324.8 nm in parallel to the sample, prepare the relation curve between the obtained absorbance and the copper amount, transfer the relation curve in parallel so as to pass the origin and take it as the working curve.

Note ⁽⁹⁾ It is to be made the same amount as the pouring amount used in 6.2.4.2.

Remarks: As to Note ⁽¹⁾ refer to Note of 5.2.4.1.

(2) In the case where gallium arsenide is used

- (a) Weigh out gallium arsenide [6.2.2 (5)] of the same amount as the weighing-out amount of sample in several pieces, and after transferring respectively into test tubes ⁽¹⁾, perform the operation of 5.2.4.1 (2).
- (b) Operate according to the procedures of (b) to (d) of 6.2.6 (1).

6.2.7 Calculation Obtain the copper amount from the absorbance obtained in 6.2.4.2 and 6.2.5 and the working curve prepared in 6.2.6, and calculate the copper content rate in the sample according to the following formula.

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

where, A_1 : copper detecting amount in sample solution (g)

A_2 : copper detecting amount in blank test solution (g)

m : weighing-out amount of sample (g)

6.3 Flameless atomic absorption spectrometry (Tungsten furnace)

6.3.1 Summary After decomposing the sample with hydrochloric acid and bromine, add ammonium chloride. Pour this solution into a tungsten furnace of flameless atomic absorption photometer, heat and measure the absorbance.

6.3.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) The hydrochloric acid (1 + 1) is in accordance with 5.2.2 (1).
- (2) Bromine
- (3) Ammonium chloride solution (100 g/l) The ammonium chloride solution (100 g/l) is in accordance with 5.3.2 (3).
- (4) Gallium (99.9999 wt % min.)
- (5) Arsenic (99.9999 wt % min.)
- (6) Gallium arsenide The gallium arsenide is in accordance with 6.2.2 (5).
- (7) Standard copper solution A (2 $\mu\text{gCu/ml}$) The standard copper solution A is in accordance with 6.2.2 (6).
- (8) Standard copper solution B (0.3 $\mu\text{gCu/ml}$) The standard copper solution B is in accordance with 6.2.2 (7).
- (9) Standard copper solution C (0.2 $\mu\text{gCu/ml}$) The standard copper solution C is in accordance with 6.2.2 (8).
- (10) Standard copper solution D (0.05 $\mu\text{gCu/ml}$) The standard copper solution D is in accordance with 6.2.2 (9).

6.3.3 Weighing-out amount of sample The weighing-out amount of sample shall be as given in Table 2 of 6.2.3.

6.3.4 Operation

6.3.4.1 Preparing of sample solution The preparing of sample solution shall be in accordance with 5.3.4.1.

6.3.4.2 Measuring of absorbance Pour a definite amount (⁴) of solution obtained in 6.3.4.1 into the tungsten furnace of flameless atomic absorption photometer to heat and measure the absorbance at wavelength 324.8 nm.

Remarks: As to Note (⁴) refer to Note of 5.2.4.2.

6.3.5 Blank test The absorbance of solution without adding standard copper solution to be obtained in working curve preparing operation of 6.3.6 shall be taken as the absorbance of blank test.

6.3.6 Preparing of working curve The preparing of working curve shall be in accordance with either one of the following.

(1) In the case where gallium and arsenic are used

- (a) Weigh out the gallium [6.3.2 (4)] of half amount of weighing-out amount of sample and the arsenic [6.3.2 (5)] of half amount in several pieces and transfer respectively into test tubes ⁽¹⁾.
- (b) After performing the operation of 5.3.4.1 (3) and (4), cool to ordinary temperature.
- (c) In the case where the weighing-out amount of sample is 0.20 g, add stepwise standard copper solution D [6.3.2 (10)] 0 to 0.3 ml and standard copper solution C [6.3.2 (9)] 1.0 to 3.0 ml (as copper 0 to 0.60 µg) and dilute with high-purity water up to the carved mark of 10 ml.

In the case where the weighing-out amount of sample is 0.10 g, add stepwise the standard copper solution B [6.3.2 (8)] 0 to 4.0 ml (as copper 0 to 1.2 µg) and dilute with high-purity water up to the carved mark of 20 ml.

- (d) Pour a definite amount ⁽¹⁰⁾ of this solution into the tungsten furnace of flameless atomic absorption photometer to heat, measure the absorbance at wavelength 324.8 nm in parallel to sample, prepare the relation curve between the obtained absorbance and the copper amount, transfer in parallel the relation curve so as to pass the origin and take it as the working curve.

Note ⁽¹⁰⁾ It is to be made the same amount as the pouring amount used in 6.3.4.2.

Remarks: As to Note ⁽¹⁾, refer to Note of 5.2.4.1.

(2) In the case where gallium arsenide is used

- (a) Weigh out gallium arsenide [6.3.2 (6)] of the same amount as the weighing-out amount of sample in several pieces, and after transferring respectively into test tubes ⁽¹⁾, perform the operation of 5.3.4.1 (2).
- (b) Operate according to the procedures of (b) to (d) of 6.3.6 (1).

6.3.7 Calculation Obtain the copper amount from the absorbance obtained in 6.3.4.2 and 6.3.5 and the working curve prepared in 6.3.6 and calculate the copper content rate in the sample according to the following formula.

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

where, A_1 : copper detecting amount in sample solution (g)

A_2 : copper detecting amount in blank test solution (g)

m : weighing-out amount of sample (g)

6.4 Inductively coupled plasma emission spectroscopy

6.4.1 Summary After decomposing the sample with hydrochloric acid and nitric acid, spray the solution into argon plasma of inductively coupled plasma emission spectrochemical apparatus and measure the emission density.

6.4.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) The hydrochloric acid (1 + 1) is in accordance with 5.2.2 (1).
- (2) Nitric acid The nitric acid is in accordance with 5.2.2 (2).
- (3) Gallium (99.9999 wt % min.)
- (4) Arsenic (99.9999 wt % min.)
- (5) Gallium arsenide The gallium arsenide is in accordance with 6.2.2 (5).
- (6) Standard copper solution A (2 $\mu\text{gCu/ml}$) The standard copper solution A is in accordance with 6.2.2 (6).
- (7) Standard copper solution B (1 $\mu\text{gCu/ml}$) Take out the stock solution (100 $\mu\text{gCu/ml}$) of 6.2.2 (6) 10.0 ml into 1000 ml one mark volumetric flask, dilute with water up to the marked line and take it as the standard copper solution B. Prepare this solution at each use.
- (8) Standard copper solution C (0.2 $\mu\text{gCu/ml}$) The standard copper solution C is in accordance with 6.2.2 (8).

6.4.3 Weighing-out amount of sample The weighing-out amount of sample shall be 0.50 g.

6.4.4 Operation

6.4.4.1 Preparing of sample solution The preparing of sample solution shall be in accordance with 5.4.4.1.

6.4.4.2 Measuring of emission intensity Spray a part of solution obtained in 6.4.4.1 into the argon plasma of inductively coupled plasma emission spectrochemical apparatus and measure the emission intensity at wavelength 324.754 nm ⁽⁸⁾.

Remarks: As to Note ⁽⁸⁾, refer to Note of 5.4.4.2.

6.4.5 Blank test The emission intensity of solution without adding standard copper solution to be obtained in working curve preparing operation of 6.4.6 shall be taken as the emission density.