

# JIS

## JAPANESE INDUSTRIAL STANDARD

### Methods for chemical analysis of tin metal

#### JIS H 1141—1993

Translated and Published

by

Japanese Standards Association

Printed in Japan

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

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## Methods for chemical analysis of tin metal

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1. Scope This Japanese Industrial Standard specifies the methods for determination of copper, lead, iron, arsenic, and antimony in tin metal which are specified in JIS H 2108.

Remarks: The following standards are cited in this Standard:

JIS H 2108 Tin metal

JIS K 0050 General rules for chemical analysis

JIS K 0115 General rules for molecular absorptiometric analysis

JIS K 0116 General rules for emission spectrochemical analysis

JIS K 0121 General rules for atomic absorption spectrochemical analysis

JIS K 8001 General rules for test methods of reagents

JIS K 8005 Reference materials for volumetric analysis

JIS Z 8401 Rules for rounding off of numerical values

2. General matters General matters common to the chemical analysis shall be in accordance with JIS K 0050, JIS K 0115, JIS K 0116, and JIS K 0121.

3. Sampling and treating of sample

3.1 Sampling Sampling shall be made as follows:

- (1) When an analytical sample is sampled from a metal, sample at least three metals for each melt number marked on the metal so as to represent the mean quality as far as possible, and take them as primary sample for analysis.
- (2) When the analytical sample is sampled in casting the metal, sample at least three cast samples for each one molten metal <sup>(1)</sup>, and take them as the primary sample for analysis.

Note <sup>(1)</sup> For the casting sample, cares shall be taken for the shape of a mold, a size, casting time, etc. in order to obtain the same quality as the metal as far as possible.

- (3) For the analytical sample, take chips from the primary sample for analysis by boring with a clean drill <sup>(2)</sup>, collect all the chips cut off, and remove iron powders or the like by using a strong magnet. Thereafter, cut them to about 5 mm or under with clean scissors, and mix thoroughly.

Note <sup>(2)</sup> For a boring position, bore the central part and a part near both end parts of the primary sample for analysis normally to the surface thereof and penetrate them to make the cut off chips obtain the same quality as the primary sample for analysis as far as possible.

- (4) When the sampling of the analytical sample can not conform to the requirements specified in (1) to (3), determine the sampling as agreed upon between the parties concerned with delivery.

3.2 Treating of sample The treating of a sample shall be as follows:

- (1) In order to prevent the analytical sample from being contaminated by foreign matters or the like, put it in a suitable glass container with a cover, and preserve by hermetically sealing it.
- (2) When there is a possibility that oil or the like sticks to the surface of the analytical sample, clean it preliminarily with ethanol, acetone or the like, and dry.
- (3) When the analytical sample is used for determination of iron, carry out preliminarily the following treatment.

Take a necessary quantity of the analytical sample into a beaker, add hydrochloric acid (1 + 5) to the extent wherein the test piece sinks, boil for 5 min by heating or heat at about 80°C for about 30 min, dissolve iron stuck to the surface or the mixed iron, and wash with water. Thereafter, wash successively with ethanol and acetone, and dry.

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

- (1) When an analytical sample is weighed out, cares shall be taken so that the analytical sample represents, as a rule, the mean composition.
- (2) When the analytical sample is weighed out, a chemical balance shall be, as a rule, used, and read to the nearest 1 mg.

4. Arrangement of analysis value

4.1 Number of analyses Analyze, as a rule, twice repetitively at the same analytical place.

4.2 Blank test On analysis, carry out a blank test, and correct the measured value.

4.3 Expression of analysis value An analysis value shall be expressed by mass %, and a numerical value shall be arranged as follows:

- (1) Calculate contents of copper, lead, iron, arsenic, and antimony down to one more place of decimal than the numerical value specified in JIS H 2108, and round off in accordance with JIS Z 8401 to the place specified in JIS H 2108.
- (2) Obtain the content of tin as follows: subtract the total sum of the contents of respective elements calculated by (1) from 100, and discard numerical value not to attain the decimal place specified in JIS H 2108.

5. Method for determination of copper

5.1 Classification of determination methods The method for determination of copper shall be in accordance with any one of the following methods:

- (1) Spectrophotometric method with bathocuproin complex after tin separation This method is applied to the sample of 0.0002 % (m/m) or over up to and including 0.001 % (m/m) in copper content.
- (2) Atomic absorption method This method is applied to the sample of 0.001 % (m/m) or over up to and including 0.05 % (m/m) in copper content. However, when tin [5.3.2 (2)] of which copper content is lower than the copper content in the sample can not be obtained, this method can not be applied.
- (3) Atomic absorption method after tin separation This method is applied to the sample of 0.0001 % (m/m) or over up to and including 0.005 % (m/m) in copper content.
- (4) Inductively coupled plasma atomic emission spectrometric method This method is applied to the sample of 0.0005 % (m/m) or over up to and including 0.10 % (m/m) in copper content. However, when tin [5.5.2 (2)] of which copper content is lower than the copper content in the sample can not be obtained, this method can not be applied.
- (5) Inductively coupled plasma atomic emission spectrometric method after tin separation This method is applied to the sample of 0.0001 % (m/m) or over up to and including 0.01 % (m/m) in copper content.

5.2 Spectrophotometric method with bathocuproin complex after tin separation

5.2.1 Summary After decomposing a sample with a mixed acid of hydrochloric acid and nitric acid, add sulfuric acid, and heat until white fume of sulfuric acid is generated. Add hydrobromic acid, and vaporize tin by heating. Thereafter, evaporate to dryness. After dissolving salts with hydrochloric acid, add hydroxylammonium chloride and tartaric acid, and regulate pH by adding ammonia. Add bathocuproin, extract the generated bathocuproin copper complex with 1-butanol, and measure the absorbance of the organic phase by using a photometer.

5.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 4)
- (2) Hydrobromic acid
- (3) Sulfuric acid (1 + 1)
- (4) Mixed acid (3 parts of hydrochloric acid and 1 part of nitric acid)
- (5) Aqueous ammonia (1 + 2)
- (6) Tartaric acid solution (100 g/l)
- (7) Hydroxylammonium chloride solution (100 g/l)
- (8) Bathocuproin-1-butanol solution Dissolve 0.2 g of bathocuproin in 1000 ml of 1-butanol.

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(9) 1-butanol

(10) Standard copper solution (2  $\mu\text{gCu/ml}$ ) After decomposing 0.100 g of copper [99.9 % (m/m) or over] in 20 ml of nitric acid (1 + 1), evaporate by heating, and make it syrupy. After allowing to cool, dissolve salts by adding 20 ml of hydrochloric acid (1 + 1). After cooling to ordinary temperature, transfer the solution into a 1000 ml volumetric flask with water, and dilute to the mark with water to make stock solution (100  $\mu\text{gCu/ml}$ ). Dilute only a necessary quantity of the stock solution accurately 50 times with water every time it is used to make the standard copper solution.

5.2.3 Weighing out quantity of sample The weighing out quantity of a sample shall be 2.00 g.

#### 5.2.4 Operation

5.2.4.1 Preparation of sample solution Prepare sample solution in accordance with the following procedure:

- (1) Weigh out a sample, and transfer it into a beaker (200 ml).
- (2) Cover with a watch glass, and decompose by adding little by little 10 ml of mixed acid. After ending violent reaction, thoroughly decompose by gently heating. After allowing to cool, wash the bottom surface of the watch glass with water, and remove the watch glass.
- (3) Add 10 ml of sulfuric acid (1 + 1), and heat until white fume of sulfuric acid is generated. After allowing to cool for several min, add 20 ml of hydrobromic acid, evaporate by heating, and generate thick white fume.
- (4) After allowing to cool for several min, add 10 ml of hydrobromic acid, heat again to evaporate to dryness.
- (5) After cooling to room temperature, add 10 ml of hydrochloric acid (1 + 4), and dissolve salts.
- (6) Add 10 ml of hydroxylammonium chloride solution and 10 ml of tartaric acid solution into the solution, and adjust pH at 5 to 6 by aqueous ammonia (1 + 2) with a pH meter.

5.2.4.2 Extraction of copper Extract copper in accordance with the following procedure:

- (1) Transfer the solution obtained in 5.2.4.1 (6) into a separating funnel (200 ml) by using water, and dilute the quantity of the solution to about 80 ml with water.
- (2) Add 10 ml of bathocuproin-1-butanol solution [5.2.2 (8)] to the solution, and mix by shaking violently for about 4 min. After separating it into two phases by standing still, discard the water phase, transfer the organic phase into a dry ground stopper test tube with graduation, and make 10.0 ml with 1-butanol.

**5.2.4.3 Measurement of absorbance** Filter a part of the organic phase obtained in 5.2.4.2 (2) by use of dry filter paper, take it into the absorption cell (10 mm) of a photometer, and measure the absorbance near 470 nm in wavelength by taking 1-butanol as contrast solution.

**5.2.5 Blank test** Carry out the same operation as that for a sample in parallel with the sample without using the sample.

**5.2.6 Preparation of working curve** Deal out 0 ml to 10.0 ml of standard copper solution [5.2.2 (10)] (0 µg to 20 µg as Cu) stepwise into several beakers (200 ml), hereafter carry out the same operation as that for a sample in parallel with the sample following the procedure of 5.2.4.1 (6) to 5.2.4.3, prepare the relation curve between the obtained absorbance and the quantity of copper, transfer the relation curve in parallel with the original relation curve so as to pass through the origin, and take that as the working curve.

**5.2.7 Calculation** Obtain the quantity of copper from two kinds of absorbance obtained in 5.2.4.3 and 5.2.5 and the working curve prepared in 5.2.6, and calculate the copper content in the sample according to the following formula:

$$\text{Copper \% (m/m)} = \frac{A_1 - A_2}{m} \times 100$$

where,  $A_1$  : copper detected quantity in sample solution (g)  
 $A_2$  : copper detected quantity in blank test solution (g)  
 $m$  : weighed out quantity of sample (g)

### 5.3 Atomic absorption method

**5.3.1 Summary** After decomposing a sample with mixed acid of hydrochloric acid and nitric acid, atomize the solution into the air-acetylene flame of an atomic absorption photometer, and measure the absorbance.

**5.3.2 Reagents** The reagents shall be as follows:

- (1) Mixed acid (3 parts of hydrochloric acid and 1 part of nitric acid)
- (2) Tin [99.99 % (m/m) or over] The copper content shall be known <sup>(3)</sup>, and also be lower than that contained in the sample.
- (3) Standard copper solution A (20 µgCu/ml) Only a necessary quantity of the stock solution (100 µgCu/ml) of 5.2.2 (10) is diluted accurately five times with water every service, to be taken as the standard copper solution A.
- (4) Standard copper solution B (10 µgCu/ml) Only a necessary quantity of the stock solution (100 µgCu/ml) of 5.2.2 (10) is diluted accurately ten times with water every service, to be taken as the standard copper solution B.

Note (3) The copper content is obtained by the atomic absorption method after tin separation of 5.4 or the inductively coupled plasma atomic emission spectrometric method after tin separation of 5.6.

5.3.3 Weighing out quantity of sample The weighing out quantity of a sample shall be 1.00 g.

#### 5.3.4 Operation

5.3.4.1 Preparation of sample solution Prepare sample solution in accordance with the following procedure:

- (1) Weigh out a sample, and transfer into a beaker (200 ml).
- (2) Cover with a watch glass, and decompose by adding little by little 20 ml of mixed acid. After ending violent reaction, thoroughly decompose by gently heating.
- (3) After cooling to ordinary temperature, wash the bottom surface of the watch glass with water, and remove the watch glass.
- (4) Transfer the solution into a 100 ml volumetric flask by using water, and dilute to the mark with water.

5.3.4.2 Measurement of absorbance Atomize a part of the solution obtained in 5.3.4.1 (4) into the air-acetylene flame of the atomic absorption photometer of which the zero point has been adjusted by using water, and measure the absorbance at 324.8 nm in wavelength.

5.3.5 Blank test The absorbance of the solution without adding standard copper solution, which is obtained by the working curve-preparing operation of 5.3.6, is taken as the absorbance of a blank test.

5.3.6 Preparation of working curve Prepare the working curve in accordance with the following procedure:

- (1) Weigh out several portions of each 1.00 g of tin [5.3.2 (2)] and transfer respectively into a beaker (200 ml).
- (2) Carry out the operation in accordance with the procedure of (2) and (3) of 5.3.4.1.
- (3) Add stepwise accurately various quantities (0  $\mu\text{g}$  to 500  $\mu\text{g}$  as copper) of respective standard copper solution A [5.3.2 (3)] and standard copper solution B [5.3.2 (4)].
- (4) Carry out the operation in parallel with the sample in accordance with the procedure of 5.3.4.1 (4) and 5.3.4.2, prepare the relation curve between the obtained absorbance and the quantity of copper, and transfer the relation curve in parallel with the original one as to pass through the origin to make the working curve.

**5.3.7 Calculation** Obtain the quantity of copper from two kinds of absorbance obtained in 5.3.4.2 and 5.3.5 and the working curve prepared in 5.3.6, and calculate the content of copper in the sample according to the following formula:

$$\text{Copper \% (m/m)} = \frac{A_1 - (A_2 - A_3)}{m} \times 100$$

where,  $A_1$  : detected quantity of copper in sample solution (g)

$A_2$  : detected quantity of copper in blank test solution (g)

$A_3$  : quantity of copper contained in 1.00 g of tin [5.3.2 (2)] (g)

$m$  : weighing out quantity of sample (g)

#### 5.4 Atomic absorption method after tin separation

**5.4.1 Summary** After decomposing a sample with the mixed acid of hydrochloric acid and nitric acid, add sulfuric acid, and heat until white fume of sulfuric acid is generated. Add hydrobromic acid. After vaporizing tin by heating, evaporate to dryness. After dissolving the salts in nitric acid, atomize the solution into the air-acetylene flame of an atomic absorption photometer, and measure the absorbance.

**5.4.2 Reagents** The reagents shall be as follows:

- (1) Nitric acid (1 + 2)
- (2) Hydrobromic acid
- (3) Sulfuric acid (1 + 1)
- (4) Mixed acid (3 parts of hydrochloric acid and 1 part of nitric acid)
- (5) Standard copper solution A (20 µgCu/ml) As described in 5.3.2 (3).
- (6) Standard copper solution B (2 µgCu/ml) As described in 5.2.2 (10).

**5.4.3 Weighing out quantity of sample** The weighing out quantity of a sample shall be 2.00 g.

#### 5.4.4 Operation

**5.4.4.1 Preparation of sample solution** Prepare sample solution in accordance with the following procedure:

- (1) Operate in accordance with the procedure of (1) to (4) of 5.2.4.1.
- (2) After cooling to room temperature, add 10 ml of nitric acid (1 + 2), and dissolve the salts.
- (3) After cooling to ordinary temperature, transfer the solution into a 25 ml volumetric flask with water, and dilute to the mark with water.

**5.4.4.2 Measurement of absorbance** Atomize a portion of the solution obtained in 5.4.4.1 (3) into the air-acetylene flame of an atomic absorption photometer of which the zero point has been adjusted by using water, and measure the absorbance at 324.8 nm in wavelength.

**5.4.5 Blank test** Carry out the same operation as that for a sample in parallel with the sample without using the sample.

**5.4.6 Preparation of working curve** Prepare a working curve in accordance with the following procedure:

- (1) Deal out various quantities of respective standard copper solution A [5.4.2 (5)] and standard copper solution B [5.4.2 (6)] (0 µl to 100 µl as copper) stepwise into several 25 ml volumetric flasks.
- (2) Add 10 ml of nitric acid (1 + 2), and dilute to the mark with water.
- (3) Atomize a portion of the solution into the air-acetylene flame of an atomic absorption photometer of which the zero point is adjusted by using water, measure the absorbance at 324.8 nm in wavelength in parallel with the sample, prepare the relation curve between the obtained absorbance and the quantity of copper, and transfer the relation curve in parallel with the original one so as to pass through the origin to make the working curve.

**5.4.7 Calculation** Obtain the quantity of copper from two kinds of absorbance obtained in 5.4.4 and 5.4.5 and the working curve prepared in 5.4.6, and calculate the content of copper in the sample according to the following formula:

$$\text{Copper \% (m/m)} = \frac{A_1 - A_2}{m} \times 100$$

where,  $A_1$  : detected quantity of copper in sample solution (g)

$A_2$  : detected quantity of copper in blank test solution (g)

$m$  : weighing out quantity of sample (g)

## 5.5 Inductively coupled plasma atomic emission spectrometric method

**5.5.1 Summary** After decomposing a sample with the mixed acid of hydrochloric acid and nitric acid, atomize the solution into the argon plasma of an inductively coupled plasma atomic emission spectrometric device, and measure the emission intensity.

**5.5.2 Reagents** The reagents shall be as follows:

- (1) Mixed acid (3 parts of hydrochloric acid and 1 part of nitric acid)
- (2) Tin As described in 5.3.2 (2).

- (3) Standard copper solution A (100  $\mu\text{gCu/ml}$ ) The stock solution (100  $\mu\text{gCu/ml}$ ) of 5.2.2 (10) is used.
- (4) Standard copper solution B (5  $\mu\text{gCu/ml}$ ) Only a necessary quantity of standard copper solution A [(3)] is diluted accurately 20 times with water each service to make the standard copper solution B.

**5.5.3 Weighing out quantity of sample** The weighing out quantity of a sample shall be 1.00 g.

#### **5.5.4 Operation**

**5.5.4.1 Preparation of sample solution** Prepare sample solution in accordance with 5.3.4.1.

**5.5.4.2 Measurement of emission intensity** Atomize a portion of the solution obtained in 5.5.4.1 into the argon plasma of an inductively coupled plasma atomic emission spectrometric device, and measure the emission intensity at 324.754 nm in wavelength <sup>(4)</sup>.

Note <sup>(4)</sup> If precision and accuracy have been confirmed, the measurement may be carried out by using other wavelength.

Further, for a device wherein higher order spectral line can be used, the higher order spectral line may be used. For a device with a background correcting mechanism, the mechanism may be used.

**5.5.5 Blank test** The emission intensity of the solution without addition of standard copper solution which is obtained in the working curve preparing operation of 5.5.6, is taken as the emission intensity of a blank test.

**5.5.6 Preparation of working curve** Prepare a working curve in accordance with the following procedure:

- (1) Weigh out several portions of each 1.00 g of tin [5.5.2 (2)], and transfer respectively to a beaker (200 ml).
- (2) Carry out the operation in accordance with (2) and (3) of 5.3.4.1.
- (3) Add stepwise accurately various quantities of respective standard copper solution A [5.5.2 (3)] and standard copper solution B [5.5.2 (4)] (0  $\mu\text{g}$  to 1000  $\mu\text{g}$  as copper).
- (4) After operating in accordance with 5.3.4.1 (4), atomize a portion of the solution into the argon plasma of an inductively coupled plasma atomic emission spectrometric device, measure the emission intensity at 324.754 nm in wavelength in parallel with the sample, prepare the relation curve between the obtained emission intensity and the quantity of copper, and transfer the relation curve in parallel with the original one so as to pass through the origin to make a working curve.

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**5.5.7 Calculation** Obtain the quantity of copper from two kinds of emission intensity obtained in 5.5.4.2 and 5.5.5 and the working curve prepared in 5.5.6, and calculate the content of copper in the sample according to the following formula:

$$\text{Copper \% (m/m)} = \frac{A_1 - (A_2 - A_3)}{m} \times 100$$

where,  $A_1$  : detected quantity of copper in sample solution (g)  
 $A_2$  : detected quantity of copper in blank test solution (g)  
 $A_3$  : quantity of copper contained in 1.00 g of tin [5.5.2 (2)] (g)  
 $m$  : weighing out quantity of sample (g)

## **5.6 Inductively coupled plasma atomic emission spectrometric method after tin separation**

**5.6.1 Summary** After decomposing a sample with the mixed acid of hydrochloric acid and nitric acid, add sulfuric acid, and heat until white fume of sulfuric acid is generated. Add hydrobromic acid. After vaporizing tin by heating, evaporate to dryness. After dissolving the salts with nitric acid, atomize the solution into the argon plasma of an inductively coupled plasma emission atomic spectrometric device, and measure the emission intensity.

**5.6.2 Reagents** The reagents shall be as follows:

- (1) Nitric acid (1 + 2)
- (2) Hydrobromic acid
- (3) Sulfuric acid (1 + 1)
- (4) Mixed acid (3 parts of hydrochloric acid and 1 part of nitric acid)
- (5) Standard copper solution A (20 µgCu/ml) As described in 5.3.2 (3).
- (6) Standard copper solution B (2 µgCu/ml) As described in 5.2.2 (10).

**5.6.3 Weighing out quantity of sample** The weighing out quantity of a sample shall be 2.00 g.

## **5.6.4 Operation**

**5.6.4.1 Preparation of sample solution** Prepare sample solution in accordance with 5.4.4.1.

**5.6.4.2 Measurement of emission intensity** Atomize a portion of the solution obtained in 5.6.4.1 into the argon plasma of an inductively coupled plasma atomic emission spectrometric device, and measure the emission intensity at 324.754 nm in wavelength (4).