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JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical
Analysis of Silver
Brazing Filler Metals**

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In the event of any doubt arising,
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Methods for Chemical Analysis of
Silver Brazing Filler Metals

Z 3901-1988

1. Scope

This Japanese Industrial Standard specifies the methods for chemical analysis of silver, copper, nickel, zinc, cadmium, tin, lithium, lead, and iron specified in JIS Z 3261.

2. General Matters

The general matters common to the methods for chemical analysis shall be in accordance with JIS K 0050 and JIS K 0121.

3. Sampling and Handling of Analysis Sample

3.1 Sampling and Preparation of Analysis Samples Sampling and preparation of analysis samples shall be carried out as follows:

- (1) In sampling and preparation of analysis samples, care shall be taken to make the samples represent the mean quality and particularly to ward off segregation, contamination, etc.
- (2) Sampling and preparation of analysis samples shall be in accordance with JIS Z 3900.

3.2 Weighing Sample Weighing the sample shall be carried out as follows:

- (1) In weighing the analysis sample, care shall be taken to obtain the mean composition by thoroughly mixing with stirring and to assure that there is no mixing of foreign matters.

Applicable Standards:

JIS H 2105-Pig Lead

JIS K 0050-General Rules for Chemical Analysis

JIS K 0121-General Rules for Atomic Absorption Spectrochemical Analysis

JIS K 8005-Standard Substances for Volumetric Analysis

JIS K 8701-Lead

JIS Z 3261-Silver Brazing Filler Metals

JIS Z 3900-Methods for Sampling of Precious Brazing Filler Metals

JIS Z 8401-Rules for Rounding off of Numerical Values

- (2) For weighing the analysis sample, a chemical balance shall be used to read out to the nearest 0.1 mg.

4. Arrangement of Analytical Value

4.1 Number of Times of Analysis Analysis shall be carried out two or more times on the same sample to confirm the results.

4.2 Expression of Analytical Value An analytical value shall be expressed as follows:

- (1) The analytical value shall be expressed by mass percentage.
- (2) Calculate the analytical values of alloyed components except lithium to two places of decimals, average not less than two analytical values and round off the mean value to one place of decimal in accordance with JIS Z 8401.
- (3) Calculate the analytical values of lithium and impurities to three places of decimals, average not less than two analytical values and round off the mean value to two places of decimals in accordance with JIS Z 8401.

5. N.B. to Analytical Operation

Matters to be attended to analytical operation shall be as follows:

- (1) The water to be used for analytical operation shall be free from chloride ion.
- (2) When absorbance is measured in atomic absorption method, an air and acetylene flame shall be used as a flame. However, when precision and accuracy are confirmed to be satisfactory, an air and water flame or other flames may be used.

6. Blank Test

In analysis, blank tests shall be carried out throughout the operation to correct the measured values.

7. Precaution for Safety

Utmost attention shall be paid to the handling of high pressure gas, ignition and extinction of flame.

Further, because of the possible generation of explosive acetylate compounds as a result of the combination of silver in the sample with acetylene used as fuel gas, measures against disasters shall be taken by washing the burner head with water at each time of use and others.

8. Methods for Determination of Silver

8.1 Classification of Determination Methods The method for determination of silver shall be in accordance with one of the following:

- (1) Sodium chloride titrimetric method (Gay-Lusac's method) This method does not apply to the sample containing tin of BAg-7, 7 A, 7 B, 18 and 21.

- (2) Ammonium thiocyanate titrimetric method (Volhard method) This method applies to the sample containing within 51 wt % of silver of BAg-1, 1 A, 2, 3, 4, 5, 6, 7 A, 7 B, 20, 20 A and 24.

- (3) Silver chloride gravimetric method

8.2 Sodium Chloride Titrimetric Method

8.2.1 Summary Resolve the sample with nitric acid, remove nitrogen oxide, carry out titration with sodium chloride standard solution, and take the point when white turbidity disappears as the end point.

8.2.2 Reagents The reagents shall be as follows:

- (1) Nitric acid (1 + 1) Nitric acid containing no chloride ion.
- (2) Sodium chloride standard solution A Dissolve 5.418 g of sodium chloride [JIS K 8005] in water, transfer it into a 1000 ml volumetric flask, and dilute it up to the marked line with water. One ml of this standard solution corresponds to 0.01 g of silver. Carry out standardization according to the following method.

Weigh out 1.000 g of silver (not less than 99.99 wt %), transfer it into a resolution bottle, and add 15 ml of nitric acid (1 + 1) to decompose the silver by heating gently. Hereinafter, operate in accordance with the procedures in 8.2.5 (2) to (4), titrate with sodium chloride standard solution, and calculate the amount of silver corresponding to 1 ml from the following formula:

$$f = \frac{G}{V_1 + \frac{V_2 - 0.1}{10}}$$

where f : amount of silver corresponding to 1 ml of sodium chloride standard solution A (g)

V_1 : amount used of sodium chloride standard solution A (ml)

V_2 : amount used of sodium chloride standard solution B (ml)

G : amount of silver weighed out (g)

The blank test shall be carried out as follows:

Take 15 ml of nitric acid (1 + 1) in a resolution bottle, and carry out the operation specified in 8.2.5 (1) and (2). Then, add sodium chloride standard solution B drop by drop, and take the total amount of standard solution having been added until white turbidity disappears as the blank test value.

- (3) Sodium chloride standard solution B Dilute the standard solution A prepared in (2) to 10 times correctly with water.

- (4) **Standard silver solution (1 mg Ag/ml)** Weigh out 0.500 g of silver (not less than 99.99 wt %), and transfer it into a beaker (300 ml). After decomposing by heating with 5 to 7 ml of nitric acid (1 + 1), subsequently heat it to remove nitrogen oxide. After cooling to ordinary temperature, transfer it into a 500 ml volumetric flask using water, and dilute up to the marked line with water. Preserve this solution in a brown bottle.

8.2.3 Devices The resolution bottle as shown in Attached Fig. 1 shall, as a rule, be used. A reagent bottle of good quality (250 ml) may be used instead.

8.2.4 Amount of Sample to Be Weighed Out Weigh out the amount of sample obtained according to the following formula depending on the silver content.

Further, in the case of unknown silver content, preliminarily examine the approximate silver content by other methods.

$$m = \frac{1000}{S} \times 100$$

where

m : amount of sample weighed out obtained by calculation (g)

S : anticipated silver content in the sample (wt %)

8.2.5 Operation The operation for determination shall be carried out according to the following procedures:

- (1) Weigh out the sample, transfer it into a resolution bottle, add 15 ml of nitric acid (1 + 1) per 1 g of sample, gradually raise the temperature to heat and decompose it quietly.
- (2) After decomposition, shake the resolution bottle slightly, then insert a bent glass tube into the bottle, and blow in air to expel nitrogen oxide. Repeat this operation several times until brown gas is no more generated and take out the bottle from the heat source to cool. Wash the inside walls of the bottle with water using a washing bottle, and add water to make the liquid amount approximately 50 ml.
- (3) Add correctly 100 ml of sodium chloride standard solution A with a pipette, stopper and mix it by shaking vigorously. After aggregating the precipitates, let it stand still till the supernatant becomes transparent⁽¹⁾.
- (4) Take off the stopper, add quietly 0.2 ml of sodium chloride standard solution B flowing down along the inside wall of the bottle from the buret. After white turbidity is generated by silver chloride⁽²⁾, stopper the bottle, mix them by vigorously shaking, and let it stand still. Repeat the above-mentioned operation until generation of white turbidity is stopped by addition of 0.2 ml of sodium chloride standard solution B.

- Notes (1) Because the generated silver chloride is liable to decomposition by sunshine, carry out this operation with the resolution bottle wrapped over in a black cloth or the like, and continue the titration thereafter as it is with light shielded.
- (2) If white turbidity is not generated then, add 0.2 ml by 0.2 ml of standard silver solution while mixing the solution with shaking to precipitate the excessive chloride ion. Even after white turbidity stops being generated, further add 0.4 ml of it in excess, and operate according to the procedures from 8.2.5 (4) downward. Where this operation is carried out, correction shall be made by subtracting the amount of silver added from the silver content obtained.

8.2.6 Calculation The silver content in the sample shall be calculated from the following formula⁽³⁾:

$$\text{Silver wt \%} = \frac{\left(V_1 + \frac{V_2 - 0.1}{10}\right) \times f}{m} \times 100$$

where V_1 : amount used of sodium chloride standard solution A (ml)

V_2 : amount used of sodium chloride standard solution B (ml)⁽⁴⁾

f : amount of silver corresponding to 1 ml of sodium chloride standard solution A (g)

m : amount of sample weighed out (g)

Notes (3) For the blank test, refer to 8.2.2 (2).

(4) The amount used of sodium chloride standard solution B shall not include the last 0.2 ml which has consummated the stoppage of generation of white turbidity.

8.3 Ammonium Thiocyanate Titration Method

8.3.1 Summary Decompose the sample with nitric acid and, after removing nitrogen oxide, add ammonium iron (III) sulfate as indicator. Then, carry out the titration with ammonium thiocyanate standard solution and take the point when the solution turns brownish pale red colour as the end point.

8.3.2 Reagents

- (1) Nitric acid (1 + 1) Nitric acid containing no chloride ion.

- (2) Ammonium thiocyanate standard solution Dissolve 4.0 g of ammonium thiocyanate in water to make 1000 ml. One ml of this standard solution corresponds to 0.005 g of silver. Carry out the standardization according to the following method.

Weigh out 0.250 g of silver (not less than 99.99 wt %), transfer it into a conical beaker (300 ml), add 15 ml of nitric acid (1 + 1), gradually raise the temperature to heat and decompose it gently.

Hereinafter, operate according to the procedures specified in 8.3.4 (2) and (3) to carry out the titration with ammonium thiocyanate standard solution, and calculate the amount of silver corresponding to 1 ml from this following formula:

$$f = \frac{G}{V}$$

where f : amount of silver corresponding to 1 ml of ammonium thiocyanate standard solution (g)

G : amount of silver weighed out (g)

V : amount used of ammonium thiocyanate standard solution (ml)

- (3) Ammonium iron (III) sulfate solution Dissolve ammonium iron (III) sulfate (12 hydrate) in water to saturate, and add nitric acid (1 + 1) dropwise until the solution turns yellow.

8.3.3 Amount of Sample to Be Weighed Out The amount of a sample to be weighed out shall be 0.5 g.

8.3.4 Operation The operation for determination shall be carried out according to the following procedures:

- (1) Weigh out the sample, transfer into a conical beaker (300 ml), and cover with a watch glass. Add 15 ml of nitric acid (1 + 1), raise the temperature gradually to heat and decompose it quietly.
- (2) Subsequently heat it to expel nitrogen oxide. After leaving cool, wash the bottom surface of the watch glass and the inside wall of the beaker with water and add water to dilute to approximately 150 ml.
- (3) Add to it 3 ml of ammonium iron (III) sulfate as indicator, while sufficiently mixing with stirring, carry out the titration with ammonium thiocyanate standard solution, and take the point when brownish pale red colour has appeared over the whole solution by the last one drop as the end point.

8.3.5 Calculation The silver content in the sample shall be calculated from the following formula:

$$\text{Silver wt \%} = \frac{V \times f}{m} \times 100$$

where V : amount used of ammonium thiocyanate standard solution (ml)

f : amount of silver corresponding to 1 ml of ammonium thiocyanate standard solution (g)

m : amount of sample weighed out (g)

8.4 Silver Chloride Gravimetric Method

8.4.1 Summary Decompose the sample with nitric acid, filter it if any precipitate exists, and add hydrochloric acid to precipitate silver. Filter it using a glass filter and, after drying, weigh its mass (use the filtrate for determination of copper).

8.4.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1 + 9)
- (2) Nitric acid (1 + 1, 1 + 100) Containing no chloride ion

8.4.3 Amount of Sample to Be Weighed Out The amount of a sample to be weighed out shall be 1.0 g.

8.4.4 Operation The operation for determination shall be carried out according to the following procedures:

- (1) Weigh out the sample, transfer it into a beaker (300 ml), cover with a watch glass, and add 10 ml of nitric acid (1 + 1). After quietly heating and decomposing, expel nitrogen oxide by boiling. Wash the bottom surface of the watch glass and of the beaker with water, and add warm water to make the liquid amount approximately 50 ml.

If then precipitates exist, leave the fluid to stand in a warm place for about 1 h, filter quickly with a filter paper (Class 5 B) containing a small amount of filter paper pulp, and wash with warm nitric acid (1 + 100).

- (2) Add water to make the liquid amount approximately 150 ml and, while mixing by stirring, add hydrochloric acid (1 + 9) little by little to generate precipitates of silver chloride. After the precipitates are no longer generated, further add 1 ml of it in excess, mix sufficiently by stirring, and heat gently for about 5 min to boil.
- (3) After leaving it as it is in a dark place overnight, filter it using a glass filter (1 G 4) preliminarily made into a constant weight, and wash it first with nitric acid (1 + 100) and next with cool water sufficiently (reserve the filtrate and washings for determination of copper).
- (4) Dry the precipitates together with the glass filter in an air bath at about 130°C for about 1 h and, after leaving to cool in a desiccator for about 1 h, weigh its mass. Repeat this operation until the mass becomes constant.

8.4.5 Calculation The silver content in the sample shall be calculated from the following formula:

$$\text{Silver wt \%} = \frac{m_1 \times 0.7526}{m_0} \times 100$$

where m_1 : mass of silver chloride (g)

m_0 : amount of sample weighed out (g)

9. Method for Determination of Copper

9.1 Method for Determination The method for determination of copper shall be in accordance with the copper electrogravimetry.

9.2 Copper Electrogravimetry

9.2.1 Summary Add sulfuric acid to the filtrate obtained in 8.4.1, heat and evaporate to generate white fumes and, after leaving to cool, add water and nitric acid to electrolyze. Weigh the mass of copper deposited on the cathode (reserve the residual liquid after electrolysis for determination of nickel, zinc or cadmium).

9.2.2 Reagents The reagents shall be as follows:

- (1) Nitric acid (1 + 1)
- (2) Sulfuric acid (1 + 1)
- (3) Ethanol (99.5 vol %)

9.2.3 Apparatus and Devices The following apparatus and devices shall, as a rule, be used.

- (1) Beaker for electrolysis (refer to Attached Fig. 2)
- (2) Platinum electrode A (refer to Attached Fig. 3)
- (3) Platinum electrode B (refer to Attached Fig. 4)
- (4) Semicircular watch glass (refer to Attached Fig. 5)

9.2.4 Operation The operation for determination shall be carried out according to the following procedures:

- (1) Add 10 ml of sulfuric acid (1 + 1) to the filtrate and washings obtained in 8.4.4 (3), heat to evaporate and generate white fumes of sulfuric acid. After leaving to cool, add about 50 ml of water and 5 ml of nitric acid (1 + 1) to dissolve the soluble salts, and expel nitrogen oxide by boiling for 1 to 2 min.
- (2) Transfer this solution into a beaker for electrolysis, add water to make the liquid amount about 150 ml. Use platinum electrode A of previously measured mass as cathode and platinum electrode B as anode, cover with two semicircular watch glasses and pass the electric current of 0.3 to 0.5 A at room temperature to electrolyze for 7 to 8 h.

- (3) Wash the bottom surfaces of the watch glasses, inside wall of beaker, and shanks of both electrodes exposed on the liquid surface with a small amount of water, allow the surface of electrolyte to rise by about 5 mm, and further continue the electrolysis for about 30 min.
- (4) When copper is no longer deposited on the shank of electrode A that is lately immersed in the electrolyte, gradually raise both the electrodes while washing with water with the current being passed, quickly immerse them in new water, remove electrode A, and wash it with water while gently moving it up and down several times⁽⁵⁾.

Immediately after washing with ethanol thoroughly, dry it quickly in an air bath at about 80°C, leave it to cool in a desiccator for about 30 min, and then weigh the mass.

Note ⁽⁵⁾ Collect residual electrolyte and washings for determination of nickel, zinc and cadmium.

9.2.5 Calculation The copper content in the sample shall be calculated from the following formula:

$$\text{Copper wt \%} = \frac{m_1}{m_0} \times 100$$

where m_1 : mass of copper deposited on electrode A (g)
 m_0 : amount of sample weighed out (g)

10. Method for Determination of Nickel

10.1 Classification of Methods for Determination The method for determination of nickel shall be in accordance with one of the following:

- (1) Dimethylglyoxime nickel gravimetric method
- (2) Dimethylglyoxime separation disodium ethylenediaminetetraacetate titrimetric method
- (3) Atomic absorptiometry (method A) This method shall be applied to the samples containing no tin compounds other than BAg-21.
- (4) Atomic absorptiometry (method B) This method shall be applied to the samples containing tin of BAg-21.

10.2 Dimethylglyoxime Nickel Gravimetric Method

10.2.1 Summary After adding tartaric acid and ammonium chloride to the residual electrolyte obtained in 9.2.1, make ammoniacal, and add dimethylglyoxime to precipitate nickel. Filter the precipitates with a glass filter and, after washing with warm water (reserve the filtrate for determination of zinc and cadmium) dry it and weigh its mass.