



JAPANESE  
INDUSTRIAL  
STANDARD

Translated and Published by  
Japanese Standards Association

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JIS K 8005 : 1999

## Reference materials for volumetric analysis

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ICS 71.040.30

**Descriptors** : chemical reagents, volumetric analysis, quantitative analysis, determination of content

**Reference number** : JIS K 8005 : 1999 (E)

K 8005 : 1999

## Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at the Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law. Consequently **JIS K 8005:1992** is replaced with **JIS K 8005:1999**.

Date of Establishment: 1951-06-26

Date of Revision: 1999-12-20

Date of Public Notice in Official Gazette: 1999-12-20

Investigated by: Japanese Industrial Standards Committee  
Divisional Council on Chemical

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JIS K 8005:1999, First English edition published in 2002-07

Translated and published by: Japanese Standards Association  
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

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Printed in Japan

## Reference materials for volumetric analysis

**1 Scope** This Japanese Industrial Standard specifies reference materials to be used for volumetric analysis.

**2 Normative references** The standards given in Attached Table 1 contain provisions which, through reference in this Standard, constitute provisions of this Standard. The most recent editions of the standards shall be applied.

**3 Items** The following 11 items are specified as reference materials for volumetric analysis.

- a) **Zinc** (Zn)
- b) **Amidosulfuric acid** ( $\text{HOSO}_2\text{NH}_2$ )
- c) **Sodium chloride** ( $\text{NaCl}$ )
- d) **Arsenic (III) oxide** ( $\text{As}_2\text{O}_3$ )
- e) **Sodium oxalate** ( $\text{NaOCOCOO}\text{Na}$ )
- f) **Sodium carbonate** ( $\text{Na}_2\text{CO}_3$ )
- g) **Copper** (Cu)
- h) **Potassium dichromate** ( $\text{K}_2\text{Cr}_2\text{O}_7$ )
- i) **Potassium hydrogen phthalate** [ $\text{C}_6\text{H}_4$  (COOK) (COOH)]
- j) **Sodium fluoride** ( $\text{NaF}$ )
- k) **Potassium iodate** ( $\text{KIO}_3$ )

### 4 General matters

**4.1 Definitions** For the main terms used in this Standard, the definitions in **JIS K 0211** and **JIS K 8001** shall apply, and the rest of the terms shall be as follows.

- a) **standard materials for volumetric analysis** Standard materials for volumetric analysis specified herein are those having the purity determined by the state and maintained and controlled by National Institute of Technology and Evaluation in the Ministry of International Trade and Industry (hereafter referred to as “standard materials”).
- b) **reference materials for volumetric analysis** Reference materials for volumetric analysis specified herein are those having the purity determined by using standard materials (hereafter referred to as “reference materials”).
- c) **purity** Purity specified herein is the ratio represented by mass % of component of a material itself.
- d) **sample stock solution** The sample stock solution is the solution containing a specific quantity of a sample which is prepared as the stock solution for sampling a necessary quantity of the sample to be used for many times.

- e) **testing solution** The testing solution is the solution containing a specific quantity of a sample which is prepared to be used for the test.
- f) **sample side solution** The sample side solution is the solution containing a sample to be used when impurities in the sample are tested by colorimetric and nephelometric analyses, which is prepared by weighing out a specific quantity of the sample necessary for the test and processed by necessary pretreatment or the like.
- g) **solution for working curve** The solution for working curve is the solution containing a specific quantity of reference solution to be used when impurities in the sample are tested by instrumental analysis. This solution is used for obtaining a line which expresses a relation with the measured value when the impurities are determined, which is prepared at the same time with the sample side solution.
- h) **reference side solution** The reference side solution is the solution containing a specific quantity of reference solution to be used when impurities in the sample are tested by colorimetric and nephelometric analyses. This solution is used as a standard when the impurities are determined, which is prepared at the same time with the sample side solution.
- i) **blank test solution** The blank test solution is the solution to be used for correction by subtracting the mixed content of a component to be determined from reagents used in the pretreatment of the sample when the impurities are determined. The solution has been processed by necessary treatment for the same quantity of reagents used for the pretreatment.

**4.2 General rules** General rules shall be in accordance with **JIS K 0050** and **JIS K 8001**.

**5 Drying conditions** Prior to use, standard materials and a sample shall be dried under the conditions specified in Table 1.

When temperature for drying is 500 °C to 600 °C, about 5 g of substance shall be weighed out in a platinum crucible, and when it is not higher than 200 °C, a necessary quantity of substance shall be taken in a flat-type weighing bottle, and its surface shall be flattened.

Further, the flat-type weighing bottle shall be of the capacity so as to make the thickness of layer of primary standard materials and samples be 5 mm or under.

For the agent for drying in a desiccator, silica gel type A class 1 specified in **JIS Z 0701** shall be used, and the cooling time in the desiccator after heating shall be 30 min to 60 min.

**Table 1 Drying condition**

| Items               | Condition                                                                                                                                                                                           |
|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Zinc                | Wash successively with hydrochloric acid (1 + 3), water, ethanol (99.5) ( <b>JIS K 8101</b> ), and diethyl ether ( <b>JIS K 8103</b> ), and immediately put in a desiccator to keep for about 12 h. |
| Amidosulfuric acid  | After crushing roughly in a mortar (made of agate), put in a vacuum desiccator to make inner pressure not more than 2.0 kPa and keep for about 48 h.                                                |
| Sodium chloride     | Heat at 600 °C for about 60 min, and allow to cool in a desiccator.                                                                                                                                 |
| Arsenic (III) oxide | Heat at 105 °C for about 2 h, and allow to cool in a desiccator.                                                                                                                                    |

**Table 1 Drying condition** (concluded)

| Items                        | Condition                                                                                                                                                                                           |
|------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sodium oxalate               | Heat at 200 °C for about 60 min, and allow to cool in a desiccator.                                                                                                                                 |
| Sodium carbonate             | Heat at 600 °C for about 60 min, and allow to cool in a desiccator.                                                                                                                                 |
| Copper                       | Wash successively with hydrochloric acid (1 + 3), water, ethanol (99.5) ( <b>JIS K 8101</b> ), and diethyl ether ( <b>JIS K 8103</b> ), and immediately put in a desiccator to keep for about 12 h. |
| Potassium dichromate         | After crushing roughly in a mortar (made of agate), heat at 150 °C for about 60 min, and allow to cool in a desiccator.                                                                             |
| Potassium hydrogen phthalate | After crushing roughly in a mortar (made of agate), heat at 120 °C for about 60 min, and allow to cool in a desiccator.                                                                             |
| Sodium fluoride              | After heating at 500 °C for about 60 min, allow to cool in a desiccator.                                                                                                                            |
| Potassium iodate             | After crushing roughly in a mortar (made of agate), heat at 130 °C for about 2 h, and allow to cool in a desiccator.                                                                                |

## 6 Testing methods for purity

**6.1 Potentiometric titration** This method is applicable to the tests of amidosulfuric acid, sodium chloride, arsenic (III) oxide, sodium oxalate, sodium carbonate, potassium dichromate, potassium hydrogen phthalate and potassium iodate.

**6.1.1 Summary** Sampling a specific amount of a standard material and sample, titrate them with the solution for titration by gravimetric buret according to the descriptions in 5 of **JIS K 0113**, and find the purity of the sample from the quantity of titrant based on the purity of the standard material.

**6.1.2 Reagents and water** Reagents and water shall conform to the following requirements.

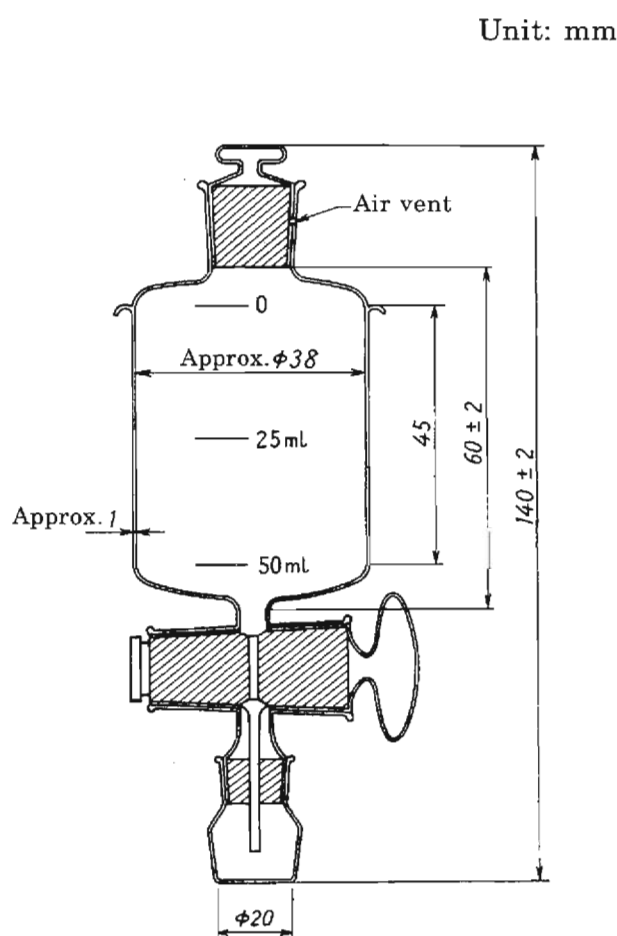
- Water** Ionic-exchange water purified by means of a quartz distilling apparatus.
- Solution for titration** The solution for titration shall be of the class and concentration specified in 6.1.5, and its preparation shall be in accordance with 4.5 of **JIS K 8001**. In this case, the standardization is not carried out.
- Nitrogen** The high purity nitrogen grade 1 specified in **JIS K 1107**.
- Oxygen-free nitrogen** The high purity nitrogen grade 1 specified in **JIS K 1107** made oxygen-free by being passed through a gas-washing bottle filled with alkaline pyrogallol solution specified in 3.6 (4) (Dissolved oxygen-free water) of **JIS K 8001**.

**6.1.3 Apparatus and appliance** Apparatus and appliance shall conform to the following:

- Gravimetric buret** Borosilicate glass buret, weighing about 60 g and about 50 ml in capacity shown in Fig. 1.
- Beaker for titration** A beaker with a ground glass cover shown in Fig. 2.

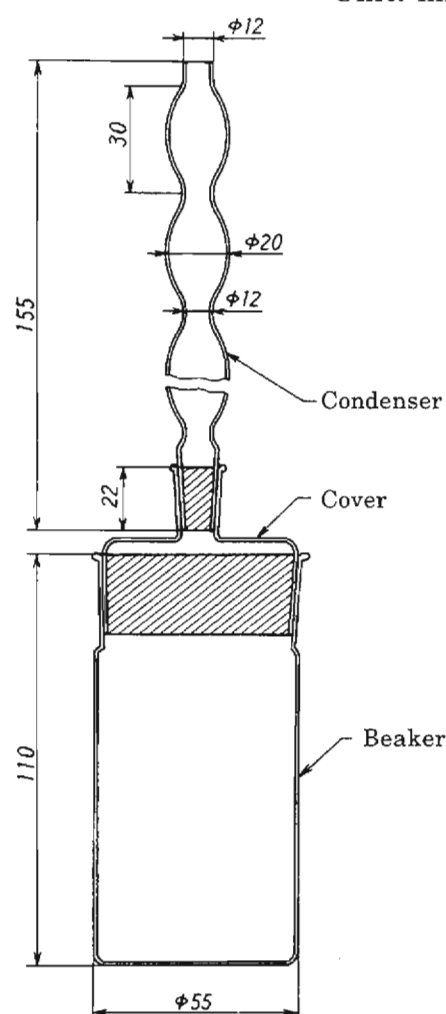
- c) **Magnetic stirrer** A stirrer that will give no influence on liquid temperature from heat by rotation.
- d) **Potentiometer** High-input resistance potentiometer capable of reading to 1 mV of potential difference.
- e) **Indicator electrode** Platinum electrode, silver electrode or glass electrode.  
Type of the electrode to be employed is specified in 6.1.5.
- f) **Reference electrode** Saturated silver chloride electrode, or saturated calomel electrode.
- g) **Microbalance** Capable of weighing to 0.01 mg difference in mass.
- h) **Chemical balance** Capable of weighing to 0.1 mg difference in mass.

Unit: mm



Remarks: The shaded part is ground joint.

**Fig. 1 An example of gravimetric buret**



Remarks: The shaded part is ground joint.

**Fig. 2 An example of beaker for titration**

**6.1.4 Common matters on operation** Common matters on operations shall be as follows:

- a) **Handling of a gravimetric buret** After washing and drying at 105 °C, reserve it in a desiccator. Prior to use, take out and allow it to stand in the room where titration will be carried out for not less than 30 min.
- b) **Handling of solution for titration** Use the solution for titration after allowing to stand in the room where titration will be carried out for not less than 1 h.
- c) **Operation for titration using a gravimetric buret** Put at least a necessary quantity of titrant into a gravimetric buret, cover, and weigh to the nearest 0.1 mg. Near the end point of titration, weigh the mass to the nearest 0.1 mg every time the titrant is added, and record each time.
- d) **Number of tests** Carry out tests seven times for the standard material and for the sample, respectively.

**6.1.5 Operation for each item** The operation for each item shall be carried out as follows.

a) **Amidosulfuric acid**

- 1) Weigh respectively from 1.4 g to 1.6 g of standard material and sample dried as indicated in **5** to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.
- 2) Dissolve in 100 ml water containing no carbon dioxide <sup>(1)</sup>.  
Note <sup>(1)</sup> Stir with a magnetic stirrer.
- 3) While passing nitrogen gas through the solution surface, titrate with 0.5 mol/l sodium hydroxide solution <sup>(1)</sup>.

Use a glass electrode as an indicator electrode.

b) **Sodium chloride**

- 1) Weigh respectively from 0.23 g to 0.25 g of standard material and sample dried as indicated in **5** to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.
- 2) Dissolve it adding 100 ml of water <sup>(1)</sup>.
- 3) Titrate with 0.1 mol/l silver nitrate solution <sup>(1)</sup>. Use silver electrode as an indicator electrode.

Connect a reference electrode to the solution to be titrated with a salt bridge <sup>(2)</sup>.

Note <sup>(2)</sup> **Preparation of a salt bridge** After dissolving 7 g of ammonium nitrate specified in **JIS K 8545** in 100 ml of water and boiling the solution, and add 3 g of agar specified in **JIS K 8263** little by little while stirring the solution. After boiling again, cool to about 80 °C, and pour into a U-shaped glass tube, and allow to stand to solidify.

c) **Arsenic (III) oxide**

- 1) Weigh out 0.19 g to 0.21 g of respective standard material and sample dried as indicated in **5** to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.

- 2) After adding 10 ml of sodium hydroxide solution (100 g/l), dissolve by warming, and wash the inside walls of the beaker with 10 ml of water. Warm again to dissolve it completely <sup>(1)</sup>.
- 3) After adding 12 ml of hydrochloric acid (2 + 1), make 100 ml by adding water.
- 4) After adding one drop of 2.5 m mol/l potassium iodate solution <sup>(3)</sup>, titrate it with 0.02 mol/l potassium permanganate solution <sup>(1)</sup>. Use a platinum electrode as an indicator electrode.

Note <sup>(3)</sup> **Preparation of 2.5-mmol/l potassium iodate solution** Mix 5 ml of 0.05 mol/l potassium iodate solution with water containing no dissolved oxygen to make totally 100 ml.

d) **Sodium oxalate**

- 1) Weigh out 0.28 g to 0.30 g of respective standard material and sample dried as indicated in 5 to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.

- 2) Dissolve by adding 100 ml of sulfuric acid (1 + 19) <sup>(1)(4)</sup>.

Note <sup>(4)</sup> Use the acid that has been boiled for 10 min to 15 min and then cooled to room temperature.

- 3) Keep the solution temperature at  $27 \pm 3$  °C, and add 0.02 mol/l potassium permanganate solution with the mass (about 40 g to 42 g) that is equivalent to about 95 % of the estimated quantity of titrant in the course of about 1 min while stirring gently.
- 4) After the red colour in the solution disappears, heat the solution up to 55 °C to 60 °C, and titrate it with 0.02 mol/l potassium permanganate solution <sup>(1)</sup> while maintaining the above temperature.

Use a platinum electrode as an indicator electrode.

e) **Sodium carbonate**

- 1) Weigh out 1.0 g to 1.2 g of respective standard material and sample dried as indicated in 5 to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.
- 2) Dissolve it adding 80 ml of water <sup>(1)</sup>.
- 3) Put a cover over the beaker, add drop by drop 0.5 mol/l hydrochloric acid with the mass (about 34 g to 41 g) that is equivalent to about 90 % of the estimated quantity of titrant from the center hole of the cover while stirring.
- 4) Attaching a condenser to the cover, boil for about 3 min. After cooling to room temperature, wash the condenser and the inside of the cover with water and detach them.
- 5) Successively, carry out titration <sup>(1)</sup> with 0.5 mol/l hydrochloric acid that has been used in 3). Use a glass electrode as an indicator electrode.

f) **Potassium dichromate**

- 1) Weigh out 0.19 g to 0.21 g of respective standard material and sample dried as indicated in 5 to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml Erlenmeyer flask <sup>(5)</sup>.

Note (5) The neck part of the Erlenmeyer flask shall have enough inside diameter to accept apparatus for titration, such as electrode, nitrogen gas introducing tube, etc. and shall also be provided with an interchangeable ground joint.

- 2) Dissolve by adding 150 ml of water containing no dissolved oxygen (1).
- 3) After displacing the air in the flask by passing the oxygen-free nitrogen gas through the solution surface, add immediately  $3.00 \pm 0.05$  g of potassium iodide specified in **JIS K 8913** and 6 ml of sulfuric acid (1 + 5), and allow to stand in a dark place for about 10 min after stoppering and stirring slowly.
- 4) Titrate with 0.1 mol/l sodium thiosulfate solution (1). Use a platinum electrode as an indicator electrode.

After the colour of the solution turns yellow, continue to titrate passing oxygen-free nitrogen gas through the solution surface.

g) **Potassium hydrogen phthalate**

- 1) Weigh out 0.8 g to 1.0 g of respective standard material and sample dried as indicated in 5 to the nearest 0.01 mg using a weighing bottle, and transfer into a 300 ml beaker for titration.
- 2) Dissolve by adding 100 ml of water containing no carbon dioxide (1).
- 3) While passing nitrogen gas through the solution surface, titrate with a 0.1 mol/l sodium hydroxide solution (1).

Use a glass electrode as an indicator electrode.

h) **Potassium iodate**

- 1) Weigh out 0.14 g to 0.16 g of respective standard material and sample dried as indicated in 5 to the nearest 0.01 mg using a weighing bottle, and transfer into an 300 ml Erlenmeyer flask (5).
- 2) Dissolve by adding 150 ml of water containing no dissolved oxygen (1).
- 3) After displacing the air in the flask by passing oxygen-free nitrogen gas through the solution surface, add immediately  $2.00 \pm 0.05$  g of potassium iodide specified in **JIS K 8913** and 5 ml of sulfuric acid (1 + 5) quickly, and allow to stand in a dark place for about 10 min after stoppering and stirring slowly.
- 4) Titrate with 0.1 mol/l sodium thiosulfate solution (1). Use a platinum electrode as an indicator electrode.

After the colour of the solution turns yellow, carry out the titration passing oxygen-free nitrogen gas through the solution surface.

**6.1.6 Calculation** Calculate the purity by using the following formula, and round off the results to obtain the significant figures fit for the standardized values in accordance with **JIS Z 8401**.

Calculate the values of  $W_i$  and  $W_{oi}$  to three decimal places.

$$P = P_0 \times \frac{\frac{\sum_{i=1}^7 W_i}{7}}{\frac{\sum_{i=1}^7 W_{oi}}{7}}$$

$$W_i = \frac{T_i}{m_i}$$

$$W_{oi} = \frac{T_{oi}}{m_{oi}}$$

where,  $P$  : purity of sample (%)  
 $P_0$  : purity of standard material (%)  
 $W_i$  : equivalent quantity of titrant per 1 g of sample (g)  
 $W_{oi}$  : equivalent quantity of titrant per 1 g of standard material (g)  
 $T_i$  : titrant for sample (g)  
 $T_{oi}$  : titrant for standard material (g)  
 $m_i$  : mass of sample (g)  
 $m_{oi}$  : mass of standard material (g)

**6.2 Gravimetric method** This method shall be applicable to sodium fluoride.

**6.2.1 Summary** Add sulfuric acid to sodium fluoride, heat, convert to sodium sulfate, weigh the mass, and calculate the purity.

**6.2.2 Appliance and apparatus** Appliance and apparatus shall conform to the following.

- a) **Platinum crucible** Either No. 30 or No. 40 specified in **JIS H 6201**.
- b) **Electric furnace** Controllable between 240 °C and 880 °C.

**6.2.3 Operation** Operations shall be carried out as follows:

- a) Weigh out 1.1 g to 1.3 g of the sample dried as indicated in **5** to the nearest 0.1 mg by using a weighing bottle and put it into a platinum crucible whose mass is already known.
- b) After moistening with a small amount of water, gently add 3 ml of sulfuric acid (1 + 1).
- c) Put a cover on the platinum crucible, and heat the crucible, with the cover slid a little, on a sand bath <sup>(6)</sup> so as to raise the temperature to about 240 °C in 40 min. Continuously maintain its temperature at the same level for 1 h further, and evaporate liberated hydrofluoric acid.

Note <sup>(6)</sup> The hot plate containing clean sand is used, and temperature is measured by inserting the thermometer into sand.

Further, quartz sand should preferably be used as the sand.

- d) Put the cover over the platinum crucible correctly, and place in an electric furnace heated already to about 240 °C. Heat it so as to raise its temperature to 480 °C to 490 °C in 50 min. Continuously maintain its temperature at the same level for about 1 h further.

- e) Then, heat more strongly so as to raise its temperature to 800 °C to 880 °C in 60 min. Continuously maintain its temperature at the same level for about 30 min further.
- f) Take the platinum crucible out of the furnace, and after cooling it in a desiccator, weigh its mass to the nearest 0.1 mg. Again heat at 800 °C to 880 °C for about 30 min and, after cooling, weigh its mass. Repeat this operation until constant mass is attained.
- g) Calculate the mass of sodium sulfate from the achieved constant mass.
- h) Carry out the test four times.

**6.2.4 Calculation** Calculate the purity by using the following formula, and round off the results to obtain the significant figures fit for the standardized values in accordance with **JIS Z 8401**.

Calculate the value of  $P'_i$  to three decimal places.

$$P = \frac{\sum_{i=1}^4 P'_i}{4}$$

$$P'_i = \frac{W \times 0.591\ 20}{m} \times 100$$

where,  $P$  : purity of sodium fluoride (%)  
 $P'_i$  : purity of sodium fluoride obtained at each test (%)  
 $W$  : mass of sodium sulfate (g)  
 $m$  : mass of sample (g)  
 0.591 20 : mass of sodium fluoride equivalent to 1 g of sodium sulfate (g)

**6.3 Subtraction method** This method shall be applicable to zinc.

**6.3.1 Summary** After the determination of each content of impurities (copper, cadmium, tin, lead and iron) in the sample of zinc, find zinc purity by subtracting the total of impurities from 100 %.

**6.3.2 Operation** Operations shall be carried out as follows.

- a) Carry out tests according to **8.2.2** and find the contents of impurities.
- b) Carry out the test three times.

**6.3.3 Calculation** Calculate the purity in accordance with the following formula, and discard the figure at third place of decimal and downward.

The content of impurities is calculated by averaging the test results and rounding off to four decimal place in accordance with **JIS Z 8401**.

$$P = 100 - (A + B + C + D + E)$$

where,  $P$  : purity(%)  
 $A$  : content of copper (%)

$B$  : content of cadmium (%)

$C$  : content of tin (%)

$D$  : content of lead (%)

$E$  : content of iron (%)

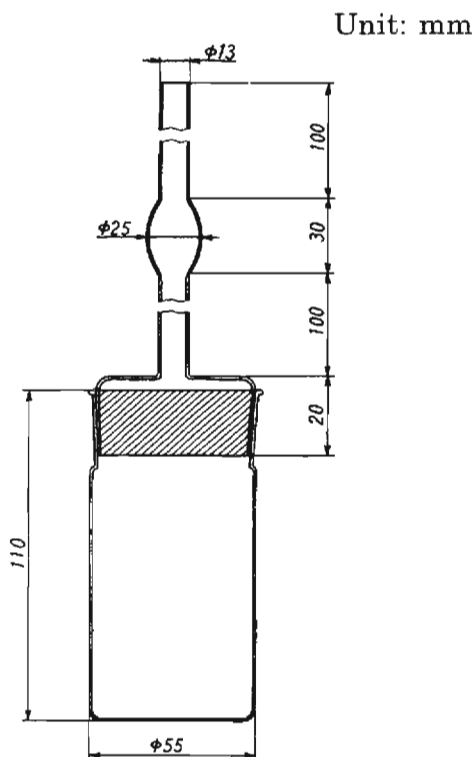
**6.4 Electrogravimetry** This method shall be applicable to copper.

**6.4.1 Summary** Dissolve copper in mixed acids of nitric acid and sulfuric acid. After adding water, electrolyze the solution by passing a specific intensity current by using a platinum electrode. Measure the mass of the electrodeposited copper.

Separately, obtain the mass of copper remaining in the residual solution of electrolyte by an atomic absorption spectrometry, and obtain the purity by correcting the quantity of electrodeposited copper.

**6.4.2 Apparatus and appliance** Apparatus and appliance shall conform to the following.

- a) **Beaker for electrolysis** Made of borosilicate glass, as shown in Fig. 3.
- b) **Cylindrical platinum cathode** Made of platinum, as shown in Fig. 4.
- c) **Spiral platinum anode** Made of platinum, as shown in Fig. 5.
- d) **Semicircular watch glass** Made of borosilicate glass, as shown in Fig. 6.
- e) **Electrolytic apparatus** The electrolytic apparatus as given in Fig. 7.



Remarks: The shaded part is ground joint.

**Fig. 3 Example of beaker for electrolysis and the cover**

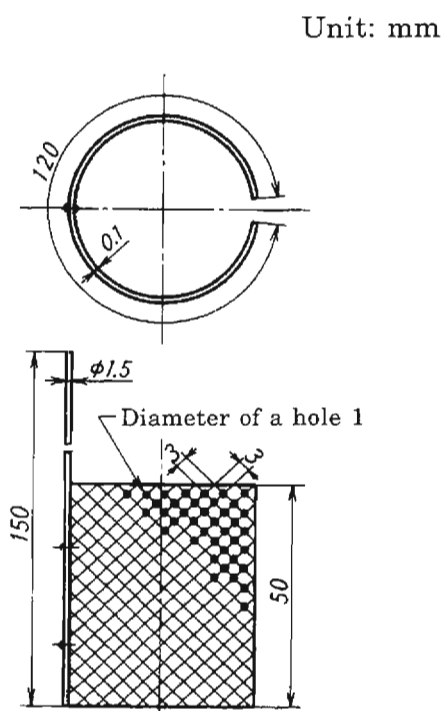


**Fig. 4 Example of cylindrical platinum cathode**

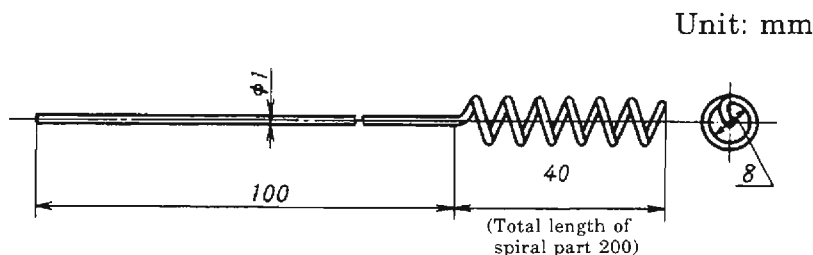


**Fig. 5 Example of spiral platinum anode**

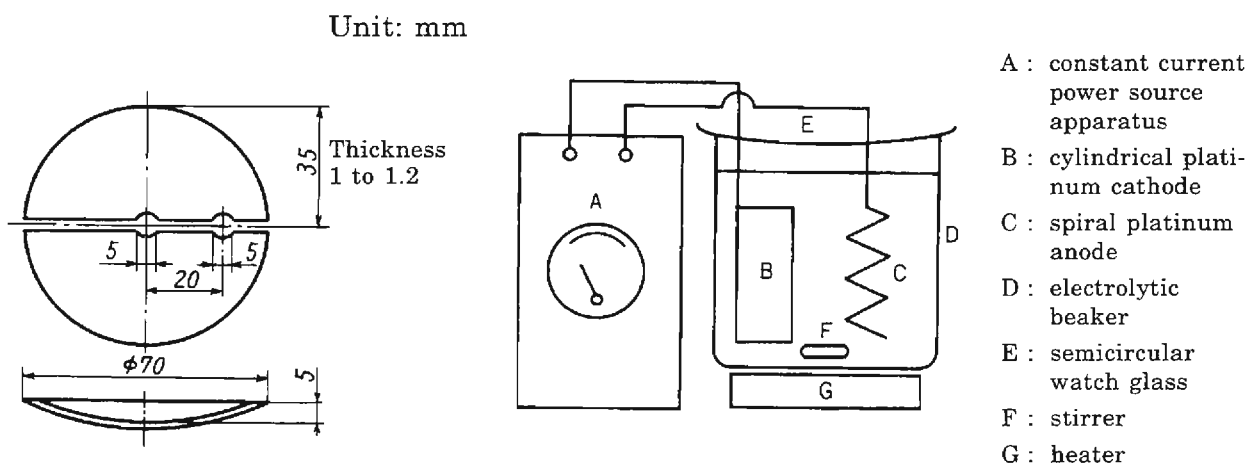


**Fig. 6 Example of semi-circular watch glass**

**Fig. 7 Principle figure of constant current electrolytic apparatus**

#### 6.4.3 Operation Operations shall be carried out as follows:

- a) Weigh out 5.000 g to 5.005 g of the sample dried as indicated in 5 to the nearest 0.1 mg. Then, weigh the mass again together with a cleaned cylindrical platinum cathode<sup>(7)</sup>. Subtract the mass of the sample from the mass of cathode plus sample, and obtain the mass of the cylindrical platinum cathode.

Note <sup>(7)</sup> Wash successively with water and then ethanol (99.5) specified in **JIS K 8101** and, after drying in a dryer kept at about 80 °C, cool it in a desiccator.

- b) Put the sample in a beaker for electrolysis, add 57 ml of mixed acids of nitric acid and sulfuric acid<sup>(8)</sup> and, after putting a cover, allow it to dissolve gradually. When the dissolution is almost over, heat it up carefully to about 80 °C to dissolve completely and to expel nitrogen oxide at the same time.

Note <sup>(8)</sup> **Preparation of mixed acids** Add gently 14 ml of nitric acid specified in **JIS K 8541** and 20 ml of sulfuric acid specified in **JIS K 8951** to 80 ml of water, and mix them.

- c) After washing the inside of the cover and the inside wall of the beaker for electrolysis with water, add water to make volume of the solution about 150 ml, and then agitate uniformly.
- d) Use the cylindrical platinum cathode and spiral platinum anode as the electrodes, and cover the beaker for electrolysis with two semicircular watch glasses. Keeping the temperature of the solution at 20 °C to 30 °C<sup>(9)</sup>, apply 0.3 A to 0.4 A of electric current for about 5 h<sup>(9)</sup>, and apply successively 0.6 A to 0.7 A for about 15 h to electrolyze it<sup>(9)</sup>.

Note <sup>(9)</sup> If necessary, use a suitable heater.

- e) When the electrolytic solution turns colourless, wash with water the underside of the semicircular watch glass, the inside wall of the beaker, and not-immersed part of the electrodes, and elevate the electrolytic solution level by about 5 mm. Then continue electrolysis for about 1 h.
- f) If no copper deposition appears on the newly dipped part of the cathode electrode, draw out the electrodes slowly while washing with water with the electric current still on. After having dipped the electrodes quickly into water of another beaker, take off the cathode and wash completely with water. Then immerse it in ethanol (99.5) specified in **JIS K 8101** kept in a beaker to eliminate moisture shaking it up and down quickly and, after drying in a dryer at about 80 °C for 2 min to 3 min, allow it to be cooled in a desiccator for about 30 min.
- g) Weigh the mass of the cylindrical platinum cathode with the deposition of copper to the nearest 0.1 mg by using a chemical balance, and obtain the mass of the deposited copper from its difference from the mass of the cylindrical platinum cathode weighed in a).
- h) Transfer all the residual solution of electrolyte into a 250 ml volumetric flask by washing, introduce the solution, which has been diluted to the mark with water, into the frame of an apparatus for atomic absorption analysis in accordance with **6** (operation method) of **JIS K 0121**, read the indication value at 324.8 nm wavelength, and obtain <sup>(11)</sup> the quantity of residual copper from the working curve <sup>(10)</sup>.

Notes <sup>(10)</sup> **Preparation of working curve** Take a series of aliquots stepwise from 0 ml to 30.0 ml of copper standard solution (0.01 mg Cu/ml) into respective 250 ml volumetric flasks and, after adding 20 ml of sulfuric acid (1 + 1) to each, dilute with water up to 250 ml. Read their indication values in parallel with the sample, and find the correlation between the indication value and copper content to plot a working curve.

<sup>(11)</sup> Store the residual solution after measuring the mass of residual copper for the test of nickel described in **8.7.2 i)**.

- i) Carry out this test four times.

**6.4.4 Calculation** Calculate the purity by using the following formula, and round off the results to obtain the significant figures fit for the standardized values in accordance with **JIS Z 8401**.

Calculate the value of  $P'_i$  to three decimal places.

$$P = \frac{\sum_{i=1}^4 P'_i}{4}$$

$$P'_i = \frac{D + R}{m} \times 100$$

where,

- $P$  : purity of copper (%)
- $P'_i$  : purity of copper obtained in each test (%)
- $D$  : mass of deposited copper (g)
- $R$  : mass of residual copper (g)
- $m$  : mass of sample (g)

## 7 Testing methods for impurities

### 7.1 Distillation testing method for nitrate and ammonium (Distillation-Indophenol blue method)

#### 7.1.1 Nitrate ( $\text{NO}_3$ )

- a) **Apparatus** The distillation apparatus as given in Fig. 8 shall be used.
- b) **Preparation of testing solution**
  - 1) **Sample solution** The sample solution for each item shall be specified in 8.
  - 2) **Solution for working curve** The solution for the working curve of each item shall be specified in 8.
- c) **Distilling operation** The distilling operation shall be carried out as follows:
  - 1) Transfer the sample solution and the solution for working curve respectively into a distillation flask A.
  - 2) Add 2 or 3 boiling tips to each distillation flask A, put 10 ml of sodium hydroxide solution (300 g/l) through an injection funnel D, wash with 10 ml of water, and close a ground cock.
  - 3) When about 75 ml of fraction containing initial distillation has flowed out by distillation, stop the distillation, and cool (discard about 75 ml of the fraction at this time.).
  - 4) Add 80 ml of water to the residual solution in the distillation flask A [or the residual solution in the distillation flask A in 7.1.2 c) 5)].
  - 5) Put absorption solution [2 ml of sulfuric acid (1 + 15) + 18 ml of water] into a receiver H. After dipping the tip of a counter flow stopper G, put 1 g of Devarda's alloy specified in **JIS K 8653** into the distilling flask A, and immediately connect it to the distillation apparatus.
  - 6) Distill again, and stop when about 75 ml of the fraction containing the initial distillation flows out.
- d) **Operation of absorptiometry** The operation shall be carried out as follows:
  - 1) Transfer about 75 ml of the fraction in c) 6) into respective 100 ml volumetric flasks, and add water to the mark. The sample side solution is referred to as solution A and the solution for working curve side as solution B.
  - 2) Take each 10.0 ml of solution A and solution B into respective 25 ml volumetric flasks, and add 1 ml of EDTA2Na solution (for indophenol blue method) and 4 ml of sodium phenoxide solution. After mixing by shaking, add 2.5 ml of sodium hypochlorite solution (about 10 g per l of available chlorine), add water to the mark, and allow to stand at 20 °C to 25 °C for about 15 min.
  - 3) Transfer a portion of the prepared solution into a 10 mm absorption cell in accordance with 5 (operation method) and 8 (determination) of **JIS K 0115**, and take blank test solution (of zero ml of standard solution of the solution B) as a contrast solution, and measure the absorbance at near 630 nm in wavelength.

- e) **Calculation** Obtain the quantity of nitrate ( $\text{NO}_3$ ) in accordance with 8.1 (working curve method) of **JIS K 0115**, and calculate the content (%) in the sample from the following formula:

$$P = \frac{A}{m} \times 100$$

where,  $P$  : content of nitrate ( $\text{NO}_3$ ) (%)  
 $A$  : measured value of nitrate ( $\text{NO}_3$ ) in sample solution (g)  
 $m$  : mass of sample (g)

### 7.1.2 Ammonium ( $\text{NH}_4$ )

- a) **Apparatus** The distillation apparatus as given in Fig. 8 shall be used.
- b) **Preparation of testing solution**
- 1) **Sample solution** The sample solution for each item shall be specified in 8.
  - 2) **Solution for working curve** The solution for working curve of each item shall be specified in 8.
- c) **Distilling operation** The distilling operation shall be carried out as follows:
- 1) Transfer the sample solution and the solution for working curve respectively into a distillation flask A.
  - 2) Add 2 or 3 boiling tips to each distillation flask A.
  - 3) Put absorption solution [2 ml of sulfuric acid (1 + 15) + 18 ml of water] into a receiver H, dip the tip of a counter flow stopper G, and connect it to a distillation apparatus.
  - 4) Put 10 ml of sodium hydroxide solution (300 g/l) through an injection funnel D, wash with 10 ml of water, and close a ground cock.
  - 5) Distill, and stop when about 75 ml of fraction containing initial distillation flows out.
- d) **Operation for absorptiometry** The operation shall be carried out as follows:
- 1) Transfer about 75 ml of the fraction in c) 5) into each 100 ml volumetric flask, and add water to the mark. The sample side solution is referred to as solution A and the solution for working curve side as solution B.
  - 2) Take each 10.0 ml of solution A and solution B into a 25 ml volumetric flask, and add 1 ml of EDTA2Na solution and 4 ml of sodium phenoxide solution. After mixing by shaking, add 2.5 ml of sodium hypochlorite solution (about 10 g/l available chlorine), add water to the mark, and allow to stand at 20 °C to 25 °C for about 15 min.
  - 3) Transfer a portion of the prepared solution into an absorption cell (optical path length: 10 mm) in accordance with 5 (operation method) and 8 (determination) of **JIS K 0115**, take the blank test solution (of zero ml of standard solution of the solution B) as a contrast solution, and measure the absorbance at near 630 nm in wavelength.

- e) **Calculation** Obtain the quantity of ammonium ( $\text{NH}_4$ ) in accordance with 8.1 (working curve method) of **JIS K 0115**, and calculate the content (%) in the sample according to the following formula:

$$P = \frac{A}{m} \times 100$$

where,  $P$  : content of ammonium ( $\text{NH}_4$ ) (%)

$A$  : measured value of ammonium ( $\text{NH}_4$ ) in sample solution (g)

$m$  : mass of sample (g)

Unit: mm

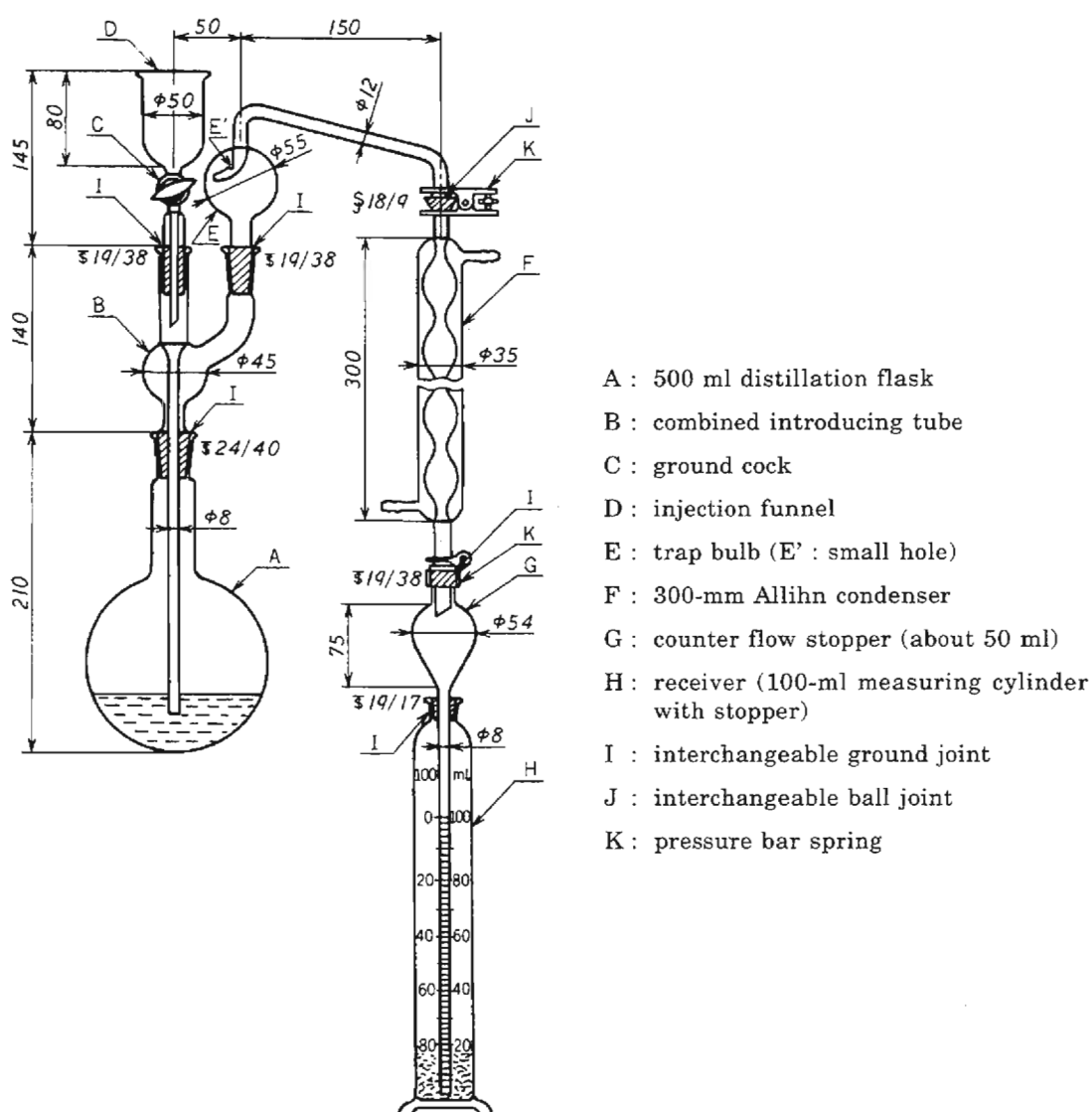


Fig. 8 Example of distillation apparatus

## 7.2 Absorptiometry

### 7.2.1 Preparation of testing solution

- a) **Sample solution** The sample solution for each item shall be specified in 8.
- b) **Solution for working curve** The solution for working curve of each item shall be specified in 8.

**7.2.2 Operation of absorptiometry** The operation shall be carried out as follows:

Transfer a portion of the prepared solution into a 10 mm absorption cell in accordance with 5 (operation method) and 8 (determination) of **JIS K 0115**, take the blank test solution (of 0 ml of the standard solution of the solution for working curve) as a contrast solution, and measure the absorbance at near the wavelength specified in 8.

**7.2.3 Calculation** Obtain the quantity of measuring objective component in accordance with 8.1 (working curve method) of **JIS K 0115**, and calculate the content (%) in the sample according to the following formula.

$$P = \frac{A}{m} \times 100$$

where,  $P$  : content of measuring objective component (%)  
 $A$  : measured value of measuring objective component  
in sample solution (g)  
 $m$  : mass of sample (g)

### 7.3 Atomic absorption spectrometry

#### 7.3.1 Preparation of testing solution

- a) **Sample stock solution** The sample stock solution for each item is specified in 8 when necessary.
- b) **Solution for working curve** The solution for working curve of each item shall be specified in 8.
- c) **Blank test solution** The blank test solution for each item is specified in 8 when necessary.

**7.3.2 Operation** The operation shall be carried out as follows:

##### a) **Solution for working curve**

- 1) After adding 2 ml of diammonium hydrogencitrate solution (100 g/l) and 2 drops or 3 drops of Bromothymol Blue solution to each solution for working curve, add little by little aqueous ammonia (2 + 3) or hydrochloric acid (2 + 1) until the solution turns from yellow to green.
- 2) Transfer into a 300 ml separatory funnel by using a small quantity of water, and further add water to make it about 200 ml in the solution.
- 3) Add 5 ml of NaDDTC solution (10 g/l) and 20 ml of butyl acetate specified in **JIS K 8377**, and mix by shaking violently for about 1 min. After allowing to stand to be separated into two layers, take the butyl acetate layer out, and transfer into a dry interchangeable ground joint Erlenmeyer flask (if necessary, equalize the quantity of each butyl acetate layer by using butyl acetate).