

JIS

JAPANESE INDUSTRIAL STANDARD

**Method for Chemical Analysis of
Oxygen-Free Copper Products
for Electron Tubes**

JIS H 1202—1982

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

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Method for Chemical Analysis of Oxygen-Free Copper Products for Electron Tubes H 1202-1982
(Reaffirmed: 1988)1. Scope

This Japanese Industrial Standard specifies method for chemical analysis of chemical components (copper, lead, zinc, bismuth, cadmium, mercury, oxygen, phosphorus sulfur, selenium and tellurium) of JIS H 3510.

2. General Items

General items common to methods for chemical analysis shall be in accordance with JIS K 0050, JIS K 0115, JIS K 0121, JIS Z 2613 and JIS Z 2616.

3. Sampling Method and Treating Method of Sample3.1 Sampling Method The sampling method shall be as follows:

- (1) The sampling method shall be, as a rule, in accordance with JIS H 0321, JIS H 1012, JIS Z 2613 and JIS Z 2616.
- (2) In case where the sampling in accordance with the abovementioned specifications is impossible, it shall be decided according to agreement between the parties concerned.

3.2 Treatment Method of Analysis Sample The treatment method of analysis sample shall be as follows:

- (1) In the case where there is a fear that the surface of sample is contaminated by oils and the like during preparation, remove by washing with ethyl alcohol, ethyl ether, etc.
- (2) In the case where there is a fear that the surface of sample is contaminated by iron content and the like, when it is able to separate by magnet or the like, remove by using magnet.

Further for sample of which contamination removal by magnet is difficult, remove contamination of iron contents and the like by carrying out the following operation.

Take a suitable amount of analysis sample into a beaker, add hydrochloric acid (1 + 10) to such degree that the pieces of sample sink, heat to boil for about 5 minutes, or dissolve iron contents and the like adhered on the surface or mixed-in by heating at about 80°C for about 30 minutes, after washing sufficiently by water, wash with ethyl alcohol and ethyl ether. After drying this by wind-blowing or naturally, dry sufficiently in a desiccator.

- (3) In the case where the surface of sample is oxidized during preparation, preliminarily the following operation shall be carried out to remove the oxide film:

Applicable Standards: See page 51.

Take a suitable amount of sample into a beaker, add acetic acid (1 + 19) to such degree the pieces of sample sink, and while mixing by shaking dissolve the copper oxide on the surface. At this time, when the degree of oxidation is high and it is difficult to clean, acetic acid (1 + 10 to 1 + 4), or potassium cyanide solution (0.1 to 1 w/v %) may be used.

When the surface of analysis sample indicates color of pure copper, immediately wash by using cool water quickly according to inclination method and further wash with ethyl alcohol, ethyl ether, etc. After drying this by wind blowing or naturally, sufficiently dry in a desiccator.

- (4) In the case where the sample for gas analysis is comparatively large such as lump, plate, bar, etc., polish the surface of sample by fine file which is rubbed preliminarily with the same metal until new metal surface appears or remove the surface of sample by electrolysis polishing.

Next wash with ethyl alcohol, ethyl ether, etc. and after drying by windblowing or naturally, preserve in a desiccator displaced by inert gas.

In the case where the sample such as wire, cut pieces, etc. is difficult in mechanical polishing of surface, prepare according to the operation of 3.2 (3).

- (5) Put the prepared sample, as a rule, into a clean glass bottle and stopper gas-tightly to preserve. When the long period preservation is required, displace the air by inert gas such as argon.

Further, because the surface of electrolysis-polished sample is active and easily oxidized, it shall not be left in air for not less than one hour.

At taking of analysis sample, mix the sample by using a clean stainless steel spoon or the like so as to hold average composition.

3.3 Weighing Method of Analysis Sample The weighing method of analysis sample shall be as follows:

- (1) For weighing out of analysis sample, use a chemical balance.
- (2) Weigh out the analysis sample for determination of pure content after drying in a desiccator for not less than one hour. However, weigh out the sample washed according to 3.2 (2) and (3) after drying in a desiccator for not less than two hours.
- (3) Weigh out the analysis sample for determination of oxygen after drying as quickly as possible since preparing, put into oxygen analysis apparatus, and hold vacuum or inert gas atmosphere.

4. Expression of Analysis Value and Cautions to Operation

4.1 Expression of Analysis Value Express the analysis value by percentage and calculate the chemical component to the next place of the significant lowest place of numerical value specified in JIS H 3510, and round off to the specified place according to JIS Z 8401.

4.2 Cautions to Operation Cautions to operation shall be as follows:

- (1) Carry out the analysis on the same sample not less than twice and affirm the results.
- (2) At analysis, carry out the blank test through the whole operation and correct the measured value.
- (3) In absorptiometry, for absorption cell of photometer, unless specially specified, use an absorption cell of 10 mm.
- (4) In atomic absorptiometry, at measuring absorbance, unless specially specified, use air-acetylene for flame. However, when having been affirmed that the precision and accuracy are satisfied, air-hydrogen and other flame may be used.
- (5) Safety and sanitation When the analysis operation is carried out, always cares shall be taken to safety and sanitation, and items to be taken specially with cares, as follows:
 - (a) In atomic absorptiometry, carry out treatment of high pressure gas, ignition and extinguishing of flame with taking cares sufficiently.
Further in analysis of oxygen and sulfur, for treatment of high pressure gas sufficiently take cares.
 - (b) For treatment of organic solvent and the like, to be accustomed with its toxicity, inflammability, explosibility and take into consideration the sufficient countermeasures.
 - (c) Cyanides have extremely strong toxicity, and therefor take care to the storage and treatment.
Further as to the treatment of waste liquid after using, take into consideration sufficiently the countermeasures.

5. Method for Determination of Copper

5.1 Division of Method The method for determination of copper shall be in accordance with electrolysis gravimetric method.

5.2 Electrolysis Gravimetric Method

5.2.1 Summary Decompose the sample with mixed acid of nitric acid and sulfuric acid and after regulating the liquid amount, pass low electric current to carry out electrolysis. After completion of electrolysis, wash the cathode with water and alcohol, then dry, and after cooling measure the electro-deposited copper amount.

For electrolysis residual liquid, obtain residual copper amount according to DDTC absorptiometry or atomic absorptiometry and correct the electro-deposition amount.

5.2.2 Reagents Reagents shall be as follows:

- (1) Sulfuric acid (1 + 1)
- (2) Mixed acid of nitric acid and sulfuric acid (nitric acid 7, sulfuric acid 10, water 40)

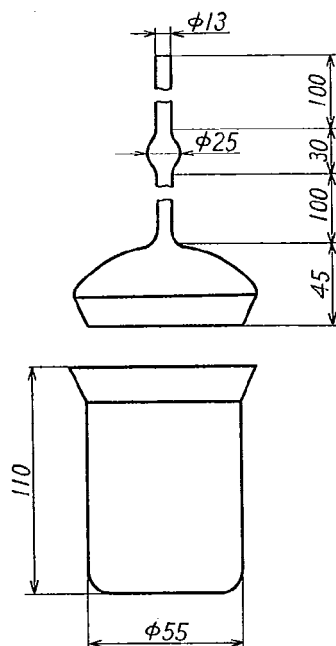
- (3) Aqueous ammonia
- (4) Ammonium citrate solution (10 w/v %)
- (5) Sodium diethyl dithio carbamate (DDTC) solution (0.1 w/v %)
If insoluble matters exist, use it with filtering. Prepare this solution at each time of use.
- (6) Ethyl alcohol (99.5 w/v %) In case of having a fear of containing free acid, after neutralization by adding a small amount of sodium hydroxide or barium hydroxide, distillate to use.
- (7) Carbon tetrachloride
- (8) Standard copper solution (10 $\mu\text{g Cu/ml}$ or 1 $\mu\text{g Cu/ml}$) Decompose copper (99.9 % min.) 0.100 g by nitric acid (1 + 1) 20 ml, after cooling transfer into a measuring flask of 1000 ml and dilute by water up to the marked line. At each time of use, dilute correctly 10 times or 100 times by only the required amount of water to make the standard copper solution.

5.2.3 Devices Devices shall be as follows:

- (1) Electrolysis beaker As a rule, use the electrolysis beaker shown in Fig. 1 and at decomposition of sample, use a cover of air cooling reflux condenser type capable of covering gas-tightly on upper part. However, when affirmed that there is no loss of copper solution in comparison with that of Fig. 1, a beaker of other type may be used.

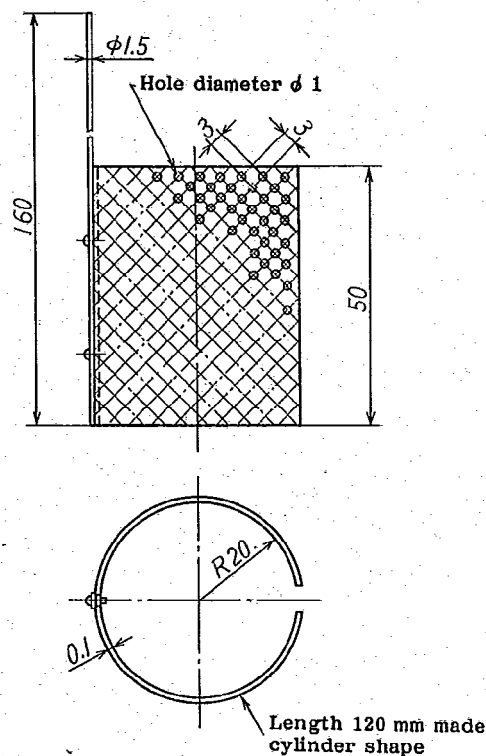
Fig. 1. Electrolysis Beaker

Unit: mm



- (2) Platinum cathode of cylinder shape As a rule, use the cathode shown in Fig. 2.

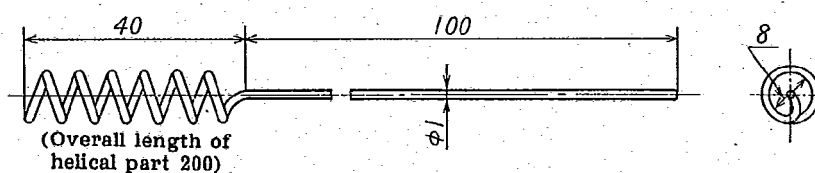
Fig. 2. Platinum Cathode of Cylinder Shape



Unit: mm

- (3) Platinum anode of helical shape As a rule, use the anode shown in Fig. 3.

Fig. 3. Platinum Anode of Helical Shape

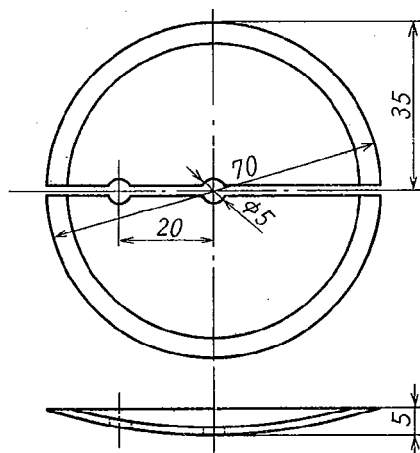


Unit: mm

- (4) Watch glass of semi-circular shape As a rule, use the watch glass shown in Fig. 4.

Fig. 4. Watch Glass of Semi-Circular Shape

Unit: mm



Thickness 1 to 1.2 mm
Material Hard glass or polyethylene

5.2.4 Weighing-out Amount of Sample Weigh out the sample 5 g to the nearest 0.1 mg⁽¹⁾.

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

- (1) Weigh out the sample, transfer into an electrolysis bottle, cover with a lid, and add mixed acid of nitric acid and sulfuric acid 57 ml to decompose gently. After stopping of decomposition reaction and carefully heat at about 80°C to decompose completely the same and at the same time expel nitrogen oxide. Next, carefully wash the inside surface of lid and inner wall of beaker, and thereafter add water to make the liquid amount about 150 ml.
- (2) By using platinum cathode of cylinder shape and platinum anode of helical shape of known mass, cover with two watch glasses of semi-circular shape, make the liquid temperature at 20 to 30°C⁽²⁾, pass electric current of 0.3 to 0.4 A for about 5 hours at first and pass electric current of 0.6 to 0.7 A for about next 15 hours to electrolyze⁽³⁾.
- (3) When electrolyte becomes colorless, wash the under surface of watch glass, inner wall of beaker, and exposed part to the liquid surface of electrodes of water, raise the electrolyte surface by about 5 mm by the washing water, and further continue electrolysis for about one hour.
- (4) When deposition of copper has become affirmed no more on the electrode newly immersed in liquid, while passing electric current and washing with water, draw up the both electrodes gradually. Next immerse quickly the cathode into new water to release it, make up and down several times to wash with water, then remove water content by ethyl alcohol, thereafter quickly dry in air bath at about 80°C, and leave cool in a desiccator for about 30 minutes.

- (5) By using the chemical balance⁽⁴⁾ used for weighing the sample, 5 g weight and weight used for weighing mass of platinum cathode, weigh the mass of platinum cathode for copper deposition.
- (6) Transfer the electrolysis residual liquid into a measuring flask, after weighing the quantity, separately take correctly 10 ml into a beaker (100 ml) from this solution, and dry to hardness by concentrating with heating. After leaving cool, add water about 30 ml to dissolve by heating, after cooling transfer into a separatory funnel (100 ml), add ammonium citrate solution 10 ml to this, after making pH 8 to 9 by using aqueous ammonia add DDTC solution 2 ml and carbon tetrachloride 10 ml accurately, mix by shaking vigorously for about one minute, stand still to separate into two layers, thereafter remove⁽⁵⁾ water content of carbon tetrachloride layer, take a part of it into an absorption cell of photometer, and measure the absorbance at nearly 440 nm in wavelength.

5.2.6 Calculation Obtain residual copper amount from working curve prepared in 5.2.7, and calculate the copper content in sample according to the following formula:

$$\text{Copper (\%)} = \frac{(W_2 - W_1) + W_3}{W} \times 100$$

where W_1 : mass of platinum cathode (g)

W_2 : mass of platinum cathode for copper deposition (g)

W_3 : residual copper amount (g)

W : weighing-out amount of sample (g)

5.2.7 Preparation of Working Curve Take various liquid amounts of standard copper solution (0 to 30 μg as copper) stepwise into several separatory funnels (100 ml), and dilute by water to about 40 ml in liquid amount. Hereinafter operate according to the procedures of adding of ammonium citrate solution of 5.2.5 (6) and thereafter, prepare the relation curve between the obtained absorbance and the copper amount to take it as the working curve.

- Notes ⁽¹⁾ Take the sample in the range of 5.0000 to 5.0050 g as far as possible. In this case, after weighing the sample, weigh the sample and platinum cathode in combination and the difference in mass between the combined amount and the sample may be taken as the mass of platinum cathode.
- ⁽²⁾ When the liquid temperature lowers than 20°C, attach a suitable temperature warming apparatus.
 - ⁽³⁾ When a faint amount of copper solution spatters according to generated gas, electrolysis at a low electric current (about 0.3 A) and for a long time (30 hours) may be carried out.
 - ⁽⁴⁾ In the case of direct indication chemical balance, use the same balance when having weighed the mass of sample and platinum cathode.
 - ⁽⁵⁾ Dehydrate by using absorbent cotton, dry filter paper, or anhydrous sodium sulfate.

Remark: The residual copper amount in residual liquid of electrolysis can be obtained by atomic absorptiometry. In this case, the operation shall be carried out as follows:

Transfer the residual liquid of electrolysis into a measuring flask of 200 ml, and dilute by water up to the marked line. By using an atomic absorption photometer, measure the absorbance at 324.7 nm in wavelength, and obtain the residual copper amount from the working curve.

Preparation of working curve: Take various liquid amounts of standard copper solution (0 to 300 μg as copper) stepwise into several measuring flasks of 200 ml, add sulfuric acid (1 + 1) 20 ml, dilute by water up to the marked line, measure in parallel with the sample, and prepare the relation curve between the obtained absorbance and the copper amount to take it as the working curve.

6. Methods for Determination of Lead

6.1 Division of Methods The method for determination of lead shall be in accordance with either one of the following methods:

- (1) Atomic absorptiometry by iron hydroxide coprecipitation separation. This method applies to the sample not less than 0.0001 % in lead content.
- (2) Atomic absorptiometry by tri-*n*-octylemethyl ammonium bromide extraction. The method applies to the sample not less than 0.00005 % in lead content.

6.2 Atomic Absorptiometry by Iron Hydroxide Coprecipitation Separation

6.2.1 Summary After decomposing the sample by nitric acid, add ammonium iron (III) sulfate, aqueous ammonia, and ammonium carbonate to coprecipitate lead and iron hydroxide and filter. After dissolving the precipitates in hydrochloric acid, dilute by water to a definite amount and measure the absorbance.

6.2.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1, 1 + 50)
- (2) Nitric acid (1 + 1)
- (3) Nitric acid mixed liquid Add hydrogen peroxide water (30 %) 10 ml to nitric acid (1 + 1) 100 ml. Prepare this solution at each time of use.
- (4) Sulfuric acid (1 + 1)
- (5) Aqueous ammonia
- (6) Ammonia washing liquid Add ammonium carbonate 15 g to aqueous ammonia (2 + 50) 500 ml to dissolve.

- (7) Hydrogen peroxide water (1 + 9)
- (8) Potassium permanganate solution (2 w/v %)
- (9) Ammonium carbonate
- (10) Ammonium persulfate
- (11) Ammonium iron (III) sulfate solution Dissolve ammonium iron (III) sulfate (24-hydrate) 10 g in nitric acid (1 + 100) to make 100 ml.
- (12) Tartaric acid solution (5 w/v %)
- (13) Standard lead solution (50 µg Pb/ml or 10 µg Pb/ml) Decompose lead (99.9 % min.) 0.110 g by nitric acid (1 + 1) 20 ml, after cooling transfer into a measuring flask of 1000 ml, and dilute by water up to the marked line. At each time of use, dilute the require amount by water correctly to two times or ten times and take it as the standard lead solution.

6.2.3 Weighing-out Amount of Sample Weigh out the sample 20 g to the nearest 10 mg.

6.2.4 Operation The operation for determination shall be carried out according to the following procedures⁽⁶⁾:

- (1) Weigh out the sample to transfer into a beaker (500 ml), cover with a watch glass, add nitric acid (1 + 1) 160 ml to decompose, then gently boil to expel nitrogen oxide and thereafter add water to make the liquid amount about 300 ml.
- (2) Add ammonium iron (III) sulfate 5 ml, while mixing by stirring add aqueous ammonia to dissolve the precipitate of copper hydroxide and thereafter further add in excess 50 ml. Next, add ammonium carbonate about 15 g, heat to boil gently for about 5 minutes, and thereafter stand as it is at a warm place⁽⁷⁾ for 1 to 2 hours.
- (3) Filter the precipitate by using filter paper (class 5 A), after washing several times by warm ammonia washing liquid, transfer with washing by warm water in the previous beaker, add dropwise hydrochloric acid (1 + 1) 10 ml from above the filter paper and dissolve the filter paper and precipitate in beaker. Wash the filter paper by warm hydrochloric acid (1 + 50) and combine the washing in the previous beaker.
- (4) Heat the solution to concentrate, after making the liquid amount about 10 ml, transfer with hydrochloric acid (1 + 50) into a beaker (100 ml), add sulfuric acid (1 + 1) 2 ml, heat to concentrate, and dry to hardness. After leaving cool, add hydrochloric acid (1 + 1) 8 ml⁽⁸⁾, heat to dissolve, after cooling transfer with hydrochloric acid (1 + 50) into a measuring flask of 25 ml and dilute up to the marked line⁽⁹⁾⁽¹⁰⁾.
- (5) By using an atomic absorption photometer measure the absorbance at 217.0 nm or 283.3 nm in wavelength.

6.2.5 Calculation Obtain the amount of lead from the working curve prepared in 6.2.6 and calculate the lead content in sample according to the following formula:

$$\text{Lead (\%)} = \frac{A}{W} \times 100$$

where A : detected amount of lead in sample solution (g)
 W : weighing-out amount of sample (g)

6.2.6 Preparation of Working Curve Take various liquid amounts of standard lead solution (0 to 200 μg as lead) stepwise into several beakers (100 ml), add ammonium iron (III) sulfate solution 5 ml and sulfuric acid (1 + 1) 2 ml, heat to concentrate and dry to hardness. Hereinafter operate according to the procedures of adding hydrochloric acid (1 + 1) 8 ml⁽¹¹⁾ of 6.2.4 (4) and thereafter, measure in parallel to the sample, prepare the relation curve between the absorbance and the amount of lead and take it as the working curve.

Notes ⁽⁶⁾ Coprecipitate with manganese, and it may be separated from copper. In this case, the operation shall be in accordance with Remark.

⁽⁷⁾ It shall be 60 to 80°C.

⁽⁸⁾ Add hydrochloric acid (1 + 1) 2 ml and tartaric acid solution 1 ml and dissolution by heating at low temperature may be carried out.

⁽⁹⁾ In the case where the lead content is large, transfer into a measuring flask of 50 ml or 100 ml so as the lead per 25 ml of liquid amount to become 50 to 200 μg . However, at this time, the adding amount of hydrochloric acid (1 + 1) shall be two times or 4 times.

⁽¹⁰⁾ From this solution, bismuth can be determined.

⁽¹¹⁾ When the operation of Note ⁽⁸⁾ is carried out, instead of hydrochloric acid (1 + 1) 8 ml, hydrochloric acid (1 + 1) 2 ml and tartaric acid solution 1 ml shall be used.

Remark: The determination of lead may be in accordance with the manganese coprecipitation separation method. In this case, the operation shall be carried out as follows:

Weigh out the sample 20.00 g, transfer into a beaker (500 ml), cover with a watch glass, add nitric acid (1 + 1) 160 ml to decompose, gently boil to expel nitrogen oxide, and thereafter add water to make the liquid amount about 200 ml. Add potassium permanganate solution 5 ml, and add dropwise hydrogen peroxide water (1 + 9) until the color of permanganic acid extinguishes. Next, add aqueous ammonia to dissolve precipitate of copper hydroxide, then further add in excess 10 ml, add ammonium persulfate 2 to 3 g, and ammonium carbonate 1 g, gently boil for about 10 minutes, thereafter filter by using filter paper (class 5 A) and wash with warm water.

Transfer the precipitate by washing with warm water into the previous beaker, add nitric acid mixed liquid 5 ml to dissolve precipitate and thereafter add warm water to make the liquid amount about 200 ml. Hereinafter repeat the reprecipitation operation further twice, then transfer the precipitate with washing by warm water into the previous beaker, and add dropwise nitric acid mixed liquid 5 ml from above the filter paper to dissolve filter paper and precipitate in beaker. Wash the filter paper with warm water, combine the washings in the previous beaker, and warm to concentrate to make the liquid amount about 10 ml. After leaving cool, transfer into a measuring flask of 25 ml, dilute by water up to the marked line⁽¹²⁾, by using an atomic absorptiometric photometer measure the absorbance at 217.0 nm or 283.3 nm in wavelength, obtain the amount of lead from the working curve and calculate the lead content in sample.

Preparation of working curve Take various liquid amounts of standard lead solution (0 to 200 µg as lead) stepwise into several measuring flasks of 25 ml, add potassium permanganate solution 5 ml and nitric acid mixed liquid 5 ml, dilute by water up to the marked line, measure in parallel to sample, and prepare the relation curve between the obtained absorbance and the amount of lead to take it as the working curve.

Note (12) From this solution bismuth and iron can be determined.

6.3 Atomic Absorptiometry by Tri-*n*-octylmethyl Ammonium Bromide Extraction

6.3.1 Summary Decompose the sample by nitric acid, carry out sulfuric acid white fume treatment to remove completely nitric acid, thereafter extract bromide complex of lead generated by adding hydrobromic acid by acetic acid-*n*-butyl containing tri-*n*-octylmethyl ammonium bromide, and by using an atomic absorptiometric photometer measure the absorbance.

6.3.2 Reagents Reagents shall be as follows:

- (1) Nitric acid (1 + 1)
- (2) Hydrobromic acid (1 + 8)
- (3) Sulfuric acid (1 + 1)
- (4) Sodium sulfate (anhydrous)
- (5) **Extraction solvent** Dilute tri-*n*-octylmethyl ammonium chloride 6 ml by acetic acid-*n*-butyl to make 40 ml. Transfer this solution into a separatory funnel (100 ml), add hydrobromic acid (1 + 8) 40 ml, mix by vigorously shaking, thereafter remove aqueous solution layer, add again hydrobromic acid (1 + 8) 40 ml, mix by vigorously shaking, then remove aqueous solution layer, dilute the organic layer by acetic acid-*n*-butyl to 5 times and take it as the extraction solvent.

- (6) Standard lead solution (10 $\mu\text{g Pb/ml}$) After decomposing lead (99.9 % min.) 0.100 g by nitric acid (1 + 1) 5 ml, add aqueous ammonia to precipitate lead as hydroxide. Filter the precipitate by using filter paper (class 5 B), and after washing by aqueous ammonia (1 + 100), dissolve by hydrobromic acid (4 + 5) 30 ml. Transfer this solution into a measuring flask of 100 ml and dilute by water up to the marked line. Standardize lead concentration of this solution according to the following operation:

Separately take this solution accurately 20 ml, transfer into a beaker (300 ml), and make the liquid amount about 100 ml by water. Add buffer solution [acetic acid (1 + 110) and sodium acetate {dissolve sodium acetate (3 water salt) 13.6 g in water to dilute to 100 ml} are mixed by equal volume] 5 ml, add kyllenol orange solution (0.1 % w/v) several drops as indicator, and thereafter add by dropping aqueous ammonia (1 + 1) until the color of solution turns red to adjust pH of solution at 4.5 to 5.0. Next, titrate by M/100 EDTA standard solution [preparation and standardization shall be in accordance with 2. (20) of JIS K 8006], allow the point when the color of solution has turned from red to yellow to be the end point, and calculate the concentration of lead according to the following formula:

$$\text{Lead concentration } (\mu\text{g/ml}) = \frac{V \times F \times 2.072}{20} \times 1000$$

where V : using amount of M/100 EDTA standard solution (ml)

F : factor of M/100 EDTA standard solution

At each time of use, dilute this solution by water correctly so as the concentration of lead to become 10 $\mu\text{g/ml}$, and take it as the standard lead solution.

6.3.3 Weighing-out Amount of Sample Weigh out the sample 3 g to the nearest 10 mg.

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

- (1) Weigh out the sample, transfer into a beaker (200 ml), cover with a water glass, add nitric acid (1 + 1) 30 ml, and gently heat to decompose. Wash the watch glass and inner wall of beaker with a small amount of water, add sulfuric acid (1 + 1) 40 ml, continue heating to generate sufficiently the white fume of sulfuric acid and to expel completely the nitric acid⁽¹³⁾.
- (2) After leaving cool, add water 70 ml, further add correctly hydrobromic acid (1 + 8) 30 ml, and gently heat to dissolve salts. After leaving cool, transfer into a separatory funnel (200 ml) and make the liquid amount 150 ml by water.
- (3) Add correctly extraction solvent 10 ml, mix by shaking vigorously for about 5 minutes, stand still to separate into two layers and remove aqueous solution layer.

- (4) Transfer the organic layer through dry filter paper or absorbent cotton into test tube with ground stopper (15 to 20 ml), and add acetic acid-*n*-butyl to make the liquid amount 10 ml⁽¹⁴⁾.
- (5) By using an atomic absorptiometric photometer measure the absorbance at 217.0 nm or 283.3 nm in wavelength⁽¹⁵⁾⁽¹⁶⁾.

Notes ⁽¹³⁾ When required, repeat the white fume treatment 2 to 3 times and remove completely nitric acid.

- ⁽¹⁴⁾ In case where the dehydration by dry filter paper or absorbent cotton is incomplete and the variation in base line is affirmed, add sodium sulfate (anhydrous) about 1 g to dehydrate completely.
- ⁽¹⁵⁾ For adjustment of zero point, use acetic acid-*n*-butyl.
- ⁽¹⁶⁾ Measuring conditions such as the most suitable flow-rate ratio of acetylene and air, and the like are different depending upon the using apparatus and therefore it is required to obtain preliminarily the most suitable conditions for each using apparatus.

6.3.5 Calculation Obtain the amount of lead from the working curve prepared in 6.3.6, and calculate the lead content in sample according to the following formula:

$$\text{Lead (\%)} = \frac{A}{W} \times 100$$

where A : detected amount of lead in sample solution (g)

W : weighing out amount of sample (g)

6.3.6 Preparation of Working Curve Take various amounts of standard lead solution (0 to 50 µg as lead) stepwise into several separatory funnels (200 ml) into which preliminarily sulfuric acid (1 + 1) 15 ml and hydrobromic acid (1 + 8) 30 ml are added correctly, and add water to make respective liquid amounts 150 ml. Hereinafter operate according to the procedures of 6.3.4 (3) and thereafter, measure in parallel to sample, and prepare the relation curve between the obtained absorbance and the lead amount to take it as the working curve.

7. Method for Determination of Zinc

7.1 Division of Method The method for determination of zinc shall be in accordance with atomic absorptiometry by tri-*n*-octyl amine extraction. This method applies to sample of not less than 0.00002 % in zinc content.

7.2 Atomic Absorptiometry by Tri-*n*-octyl amine Extraction

7.2.1 Summary Decompose the sample by nitric acid, carry out sulfuric acid white-fume treatment to remove nitric acid, thereafter extract zinc by MIBK containing tri-*n*-octyl amine as hydrochloric acid acidic solution, and by using atomic absorptiometric photometer measure the absorbance.

7.2.2 Reagents Reagents shall be as follows:

- (1) Hydrochloric acid (1 + 1) Add extraction solvent 50 ml to hydrochloric acid (1 + 1) 1 l, and mix by shaking for about 5 minutes to refine.
- (2) Nitric acid (1 + 1)
- (3) Sulfuric acid (1 + 1)
- (4) Extraction solvent Dissolve tri-*n*-octyl amine 2 ml in methyl-isobutylketon (MIBK)⁽¹⁷⁾ to dilute to 100 ml.
- (5) Standard zinc solution (1 µg Zn/ml) Decompose zinc (99.9 % min.) 0.100 g by hydrochloric acid (1 + 1) 5 ml, after cooling transfer into a measuring flask of 1000 ml, and dilute by water up to the marked line. At each time of using, dilute the required amount by water correctly to 100 times and take it as the standard zinc solution.

7.2.3 Weighing-out Amount of Sample Weigh out the sample 2 g to the nearest 10 mg.

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

- (1) Weigh out the sample to transfer into a quartz beaker (100 to 200 ml), cover with a watch glass, add nitric acid (1 + 1) 10 ml, and gently heat to decompose. Wash the watch glass and inner wall of beaker by a small amount of water, add sulfuric acid (1 + 1) 20 ml, continue heating to generate white fume of sulfuric acid sufficiently to remove nitric acid.
- (2) After leaving cool, add hydrochloric acid (1 + 1) 40 ml to dissolve salts, then transfer into a separatory funnel (200 ml) and make the liquid amount 100 ml⁽¹⁸⁾ by water.
- (3) Add extraction solvent 5 ml, mix by shaking vigorously for about 5 minutes, stand still to separate into two layers, thereafter transfer the aqueous solution layer into other separatory funnel (200 ml), add extraction solvent 5 ml, mix by shaking vigorously for about 5 minutes, stand still to separate into two layers and remove the aqueous solution layer.
- (4) Transfer the organic layer through dry filter paper or absorbent cotton into a test tube with ground stopper (15 to 20 ml) to combine, and add MIBK⁽¹⁹⁾ to make a definite amount⁽²⁰⁾⁽²¹⁾.
- (5) By using an atomic absorptiometric photometer measure the absorbance at 213.9 nm in wavelength⁽¹⁶⁾⁽²²⁾.

7.2.5 Calculation Obtain amount of zinc from the working curve prepared in 7.2.6, and calculate the zinc content in sample according to the following formula:

$$\text{Zinc (\%)} = \frac{A}{W} \times 100$$

where A : detected amount of zinc in sample solution (g)

W : weighing-out amount of sample (g)

7.2.6 Preparation of Working Curve Take various amounts of liquid of standard zinc solution (0 to 3 μg as zinc) stepwise into several separatory funnel (200 ml) into which preliminarily sulfuric acid (1 + 1) 20 ml and hydrochloric acid (1 + 1) 40 ml are added, and make the liquid amount 100 ml⁽¹⁸⁾ by water. Hereinafter operate according to the procedures of 7.2.4 (3) and thereafter, measure in parallel to the sample, and prepare the relation curve between the obtained absorbance and the amount of zinc to take it as the working curve.

Notes ⁽¹⁷⁾ Instead of MIBK, acetic acid-*n*-butyl may be used.

⁽¹⁸⁾ The liquid amount shall be free from difference between respective separatory funnels, as far as possible.

⁽¹⁹⁾ In the case of employing Note ⁽¹⁷⁾, instead of MIBK acetic acid-*n*-butyl shall be used.

⁽²⁰⁾ Usually, it shall be a definite amount between 10 to 15 ml.

⁽²¹⁾ From this solution, cadmium can be determined according to atomic absorptiometry.

⁽²²⁾ For adjustment of zero point, use MIBK [However in the case of employing Note ⁽¹⁷⁾, use acetic acid-*n*-butyl].

8. Method for Determination of Bismuth

8.1 Division of Methods The method for determination of bismuth shall be in accordance with either one of the following:

- (1) Absorptiometry by tri-*n*-octyl amine extraction This method applies to the sample not less than 0.00005 % in bismuth content.
- (2) Atomic absorptiometry by tri-*n*-octyl methyl ammonium bromide extraction This method applies to the sample of not less than 0.00002 % in bismuth content.

8.2 Absorptiometry by Tri-*n*-octyl amine Extraction

8.2.1 Summary Decompose the sample by nitric acid, after adjusting pH at 2.0 to 2.2 by sodium hydroxide, add hydrobromic acid, extract bromide complex of bismuth by benzene containing tri-*n*-octyl amine and measure its absorbance.

8.2.2 Reagents Reagents shall be as follows:

- (1) Nitric acid (1 + 1)
- (2) Hydrobromic acid (1 + 8, 1 + 89)
- (3) Sodium hydroxide solution (20 w/v %, 1 w/v %)