

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical
Analysis of Electrolytic
Cathode Copper**

JIS H 1101—1990

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JAPANESE INDUSTRIAL STANDARD

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Methods for Chemical Analysis of
Electrolytic Cathode Copper

H 1101-1990

1. Scope

This Japanese Industrial Standard specifies the methods for the determination of copper, arsenic, antimony, bismuth, lead, iron, and sulfur specified in JIS H 2121.

2. General Matters

General matters common to methods for chemical analysis shall be in accordance with JIS K 0050, JIS K 0115, JIS K 0116, JIS K 0121, JIS K 0124, and JIS Z 2616.

3. Sampling and Treating of Analytical Sample3.1 Sampling The sampling shall be as follows.

- (1) The position of which a sample is sampled shall be the central part of copper and a part near the peripheral part so that the taken sample represents the quality of the copper. Boring is performed at right angles to the surface of the copper to be generated, and sample chips shall be sampled.
- (2) Before boring, clean the tools such as drills with ethanol, acetone, etc.
When boring the sampling position after cleaning, avoid exidization of chips as far as possible without use of lubricants such as oils. In this case, control the pressure and rotational speed of the drill to prevent heat generation, but do not pour water or the like for cooling.
- (3) In the case where sample chips are of a string form, after cutting to about 10 mm or under by using clean scissors, etc., they shall be sufficiently mixed. However, the sample to be used for the determination of sulfur shall be a fine cut piece of about 2 mm or under.
- (4) All the cut samples are collected. After carefully removing iron by using a strong magnet, they are mixed to be taken as an analytical sample.
- (5) In the case where the sampling and preparation of the analytical sample cannot satisfy the requirements specified in above-mentioned (1) to (4), they shall be determined subject to the agreement between the parties concerned with delivery.

Applicable Standards and Corresponding International Standards: See page 61.

3.2 Treating of Sample The treating of sample shall be as follows.

- (1) An analytical sample shall be preserved by sealing in a suitable stopper-fitted glass (case) in order to be prevented from contamination with foreign matter, etc.
- (2) When there is the possibility of sticking of oil or the like on the surface of the analytical sample, the analytical sample shall be washed beforehand with ethanol, acetone, etc. to be dried.
- (3) When the analytical sample is used for the determination of copper, the following treatment shall be performed beforehand.

Take a necessary amount of the analytical sample into a beaker, add acetic acid (1+50) to the extent of making a test piece sink, and dissolve copper oxide on the surface with mixing by shaking. When the copper oxide on the surface is difficult to be dissolved since highly oxidized in this case, use acetic acid (1+19 to 1+4). While the surface of the sample turns rose, immediately wash quickly with water by a decantation method. Thereafter, wash successively with ethanol and acetone. Dry this by blowing or spontaneously. After allowing to stand in a desiccator for 2 to 3 hours, weigh out the analytical sample.

- (4) When the analytical sample is used for the determination of iron, the following treatment shall be performed beforehand.

Take a necessary amount of the analytical sample into a beaker, add hydrochloric acid (1+10) to the extent of making the test piece sink, boil by heating for about 5 min, or otherwise heat at about 80°C for about 30 min, and dissolve the iron stuck on the surface or contaminated. After washing with water, wash successively with ethanol and acetone and dry.

3.3 Weighing of Sample The weighing of sample shall be as follows.

- (1) When an analytical sample is weighed out, take caution so that it represents a mean composition.
- (2) For weighing out the analytical sample, use, as a rule, a chemical balance.

4. Arrangement of Analytical Value

4.1 Number of Analyses As a rule, perform the twice repeated analyses in the same analytical laboratory.

4.2 Blank Test On analysis, perform the blank test and correct for the measured values.

4.3 Expression of Analytical Value Express the analytical value by mass percentage, calculate to the next place of the significant minimum place of the numerical value specified in JIS H 2121, and round off in accordance with JIS Z 8401.

5. Method for Determination of Copper

5.1 Determination Method The method for determination of copper shall be in accordance with the copper electrogravimetric method. This method shall apply to the sample of 99.9 wt % or over in copper content.

5.2 Copper Electrogravimetric Method

5.2.1 Summary After decomposing a sample with the mixed acid of nitric acid and sulfuric acid, electrolyze by using a platinum electrode, deposit copper on the cathode, and measure the mass.

Determine copper in electrolytic residual liquid by an atomic absorption method or an inductive coupling plasma emission spectral method, obtain the amount of the copper, and correct the amount of the deposited copper.

5.2.2 Reagents The reagents shall be as follows.

- (1) Sulfuric acid (1+1)
- (2) Mixed acid (7 volume of nitric acid, 10 volume of sulfuric acid, and 40 volume of water)
- (3) Ethanol (99.5)
- (4) Standard copper solution (20 $\mu\text{gCu/ml}$) Decompose 0.100 g of copper (99.9 wt% or over) with 20 ml of nitric acid (1+1). After cooling to ordinary temperature, transfer it into a 1000 ml volumetric flask by using water, and dilute it with water to the mark line to prepare stock solution (100 $\mu\text{g Cu/ml}$). Dilute only the necessary amount thereof accurately 5 times with water on each use to prepare the standard copper solution.

5.2.3 Instruments The instruments shall be as follows.

- (1) Electrolytic beaker As a rule, use the electrolytic beaker ⁽¹⁾ given in Figure 1. When a sample is decomposed, use an air cooling reflux condenser type of cover capable of being stuck fast to its upper part.
- (2) Cylindrical platinum cathode As a rule, use a cylindrical platinum cathode given in Figure 2.
- (3) Spiral platinum anode As a rule, use a spiral platinum anode given in Figure 3.
- (4) Semicircular watch glass As a rule, use a semicircular watch glass given in Figure 4.

Note ⁽¹⁾ When no loss of copper solution has been confirmed, the other type of beaker can be used, as compared with ones given in Figure 1.

Figure 1. Example of Electrolytic Beaker

Unit: mm

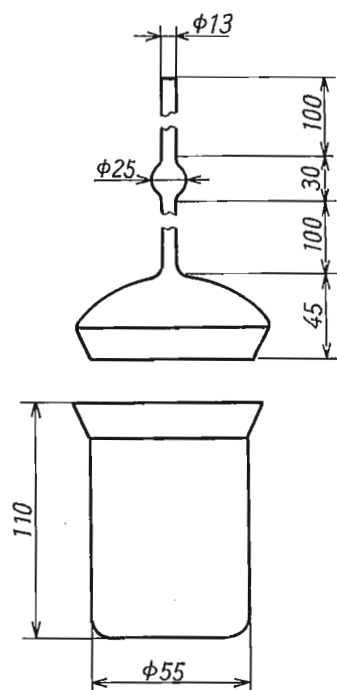


Figure 2. Example of Cylindrical Platinum Cathode

Unit: mm

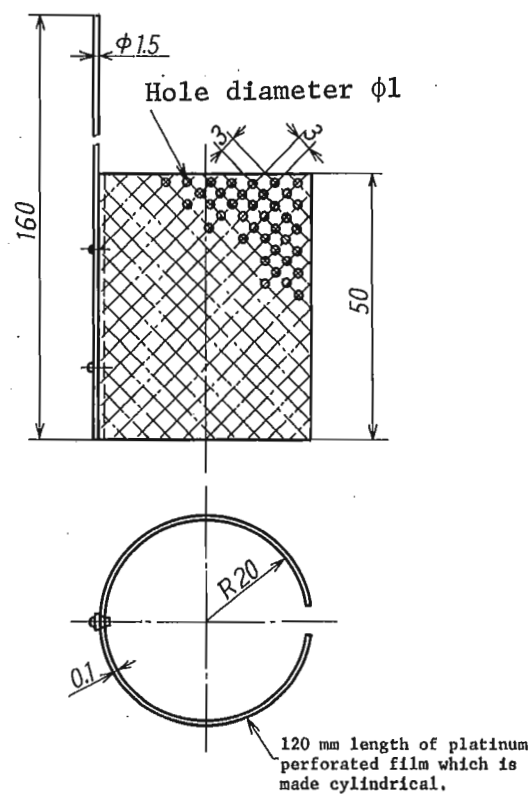


Figure 3. Example of Spiral Platinum Anode

Unit: mm

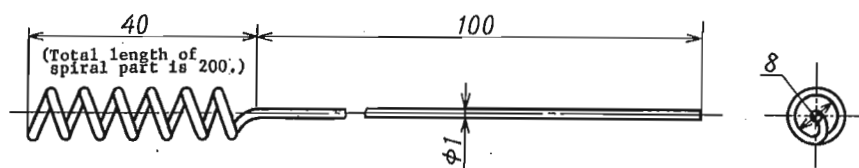
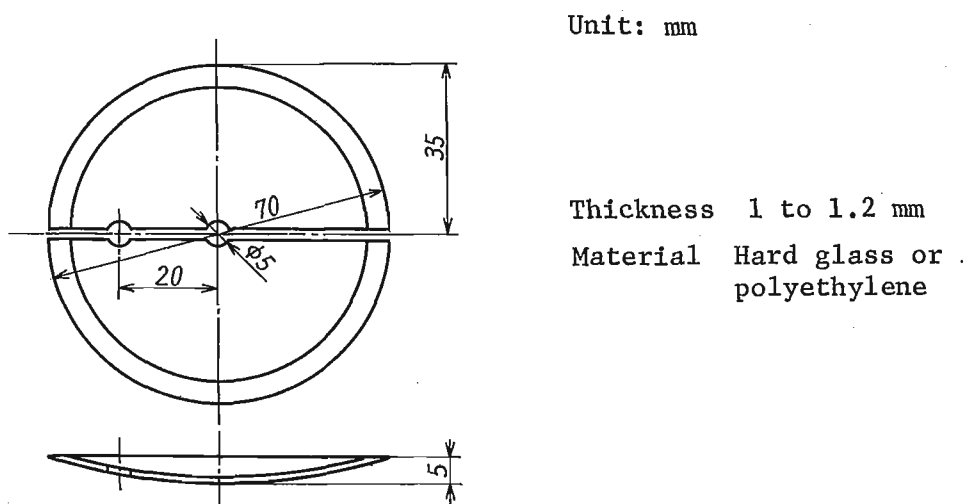


Figure 4. Semicircular Watch Glass (an Example)



5.2.4 Weighing out Amount of Sample The weighing out amount of sample shall be 5.000 g or over up to and including 5.005 g and the sample shall be weighed out to the nearest 0.1 mg ⁽²⁾.

Note ⁽²⁾ For weighing out a sample, a weighing bottle, etc. of which the mass is near the mass of the cylindrical platinum cathode [5.2.3 (2)] shall be used. In the case where a direct-reading balance is used, the sample shall be made capable of being weighed out with the display window of which the indication is as same as in 5.2.5.4.

5.2.5 Procedure

5.2.5.1 Preparatory Procedure After washing a cylindrical platinum cathode [5.2.3 (2)] by dipping in nitric acid (1+1), wash by using water and then wash by using ethanol (99.5). After drying in an air bath at about 100°C, heat with a burner to red heat. After allowing to stand to cool to room temperature in a desiccator, weigh out its mass to the nearest 0.1 mg.

5.2.5.2 Preparation of Sample Solution Prepare sample solution as follows.

- (1) Weigh out a sample and transfer it into an electrolytic beaker [5.2.3 (1)].
- (2) Cover with the cover [5.2.3 (1)], and gently decompose by adding 57 ml of mixed acid [5.2.2 (2)]. After the reaction has become quiet, heat up to about 80°C, decompose thoroughly the sample, and besides expel nitrogen oxide ⁽³⁾.
- (3) After washing the inside surface of the cover and the inside wall of the beaker with water, remove the cover and add water to make the amount of solution to about 150 ml.

Note (3) For heating, it is preferable to use a water bath or an electric hot plate which the temperature is easily regulated.

5.2.5.3 Electrolysis Perform electrolysis as follows.

- (1) Insert both the cylindrical platinum cathode [5.2.3 (2)] of which the mass was weighed out in 5.2.5.1 and the spiral platinum anode [5.2.3 (3)] into the solution obtained in 5.2.5.2 (3); and cover them with two semicircular watch glasses [5.2.3 (4)].
- (2) In keeping the temperature of the solution at 20 to 30°C (4), conduct a current of 0.3 to 0.4 A for initial about 5 hours and a current of 0.6 to 0.7 A for subsequent about 15 hours to perform electrolysis (5).
- (3) When the electrolyte becomes colorless, wash the under surface of the semicircular watch glasses, the inside wall of the beaker and the part exposed above the solution surface of the electrodes with water; raise the surface of the electrolyte by about 5 mm with the above washing water and further continue to electrolyze for about an hour.
- (4) When any more copper deposition is not observed on the handle of the cathode dipped newly in the electrolyte (6), remove the semicircular watch glasses, and gradually draw up both electrodes while conducting a current and washing them with water. Then, quickly dip the cathode into another beaker newly filled with water and separate it from the joint part. Reserve the solution after electrolysis as the electrolytic residual solution.
- (5) Preliminarily prepare two beakers newly filled with water, successively dip the cathode, and wash it with water by quickly moving it vertically. Then, preliminarily prepare two beakers filled with ethanol (99.5), successively dip the cathode therein, and remove water by moving it vertically.

Notes (4) When the temperature of the solution is lower than 20°C, attach a suitable heater.

(5) Electrolysis may be performed for a long time (about 30 hours) by a low current (about 0.3 A).

(6) When copper is deposited on the handle of the cathode dipped newly in the solution, repeat the procedure of 5.2.5.3 (3).

5.2.5.4 Drying and Weighing Dry the copper deposited platinum cathode obtained in 5.2.5.3 (5) in an air bath at about 80°C for 2 to 3 minutes and allow it stand to cool in a desiccator for about 30 minutes. Measure the mass of the copper deposited platinum cathode to the nearest 0.1 mg by using the chemical balance (7) and the 5 g weight which are used in weighing the sample and besides by using the weight used in weighing the mass of the cylindrical platinum cathode [5.2.3 (2)].

Note (7) In the case of a direct-reading chemical balance, use the same balance as that when the sample and the mass of the platinum cathode have been weighed out.

5.2.5.5 Determination of Copper in Electrolytic Residual Solution
The determination of copper in electrolytic residual solution shall be in accordance with either of the following methods.

- (1) In the Case of Determination by Atomic Absorption Method Transfer the electrolytic residual solution obtained in 5.2.5.3 (4) into a 200 ml volumetric flask by using water, and dilute it to the mark line with water. Spray a portion of this solution into air-acetylene flame of the atomic absorption photometer of which the zero point has been regulated by using water, measure the absorbance at 324.7 nm of wavelength, and obtain the amount of copper from the working curve.

Preparation of Working Curve: Take stepwise 0 to 25.0 ml of standard copper solution [5.2.2 (4)] (0 to 500 µg as copper) into several 200 ml volumetric flasks, and 20 ml of sulfuric acid (1+1), dilute it to the mark line with water, measure the absorbance while operating in parallel with the sample, prepare the relation curve between the obtained absorbance and the amount of copper, and transfer the relation curve in parallel so as to pass through the origin to be taken as the working curve.

- (2) In the Case of Determination by Inductively Coupled Plasma Emission Spectral Method Transfer the electrolytic residual solution obtained in 5.2.5.3 (4) into a 200 ml volumetric flask by using water and dilute it to the mark line with water. Spray a portion of this solution into the argon plasma of an inductively coupled plasma emission spectral apparatus, measure emission intensity of 324.754 nm in wavelength (8), and obtain the amount of copper from the working curve.

Preparation of Working Curve: Take 0 to 25.0 ml of standard copper solution [5.2.2 (4)] (0 to 500 µg as copper) stepwise into several 200 ml volumetric flasks, add 20 ml of sulfuric acid (1+1), dilute it to the mark line with water, measure emission intensity while operating in parallel with the sample, prepare the relation curve between the obtained emission intensity and the amount of copper, and transfer the relation curve in parallel so as to pass through the origin to be taken as the working curve.

Note (8) When precision and accuracy have been confirmed, other wavelengths may be used for measurement. The higher-order of spectral line may be used for the apparatus capable of using the higher-order of spectral line, and further the background correcting mechanism may be used for the apparatus equipped with the background correcting mechanism.

5.2.6 Blank Test The blank test shall not be performed.

5.2.7 Calculation The content of copper in the sample shall be calculated by the following formula.

$$\text{Copper wt \%} = \frac{(m_2 - m_1) + A}{m} \times 100$$

where m_1 : mass of cylindrical platinum cathode obtained in 5.2.5.1 (g)

m_2 : mass of copper deposited platinum cathode obtained in 5.2.5.4 (g)

A : detected amount of copper in electrolytic residual solution obtained in 5.2.5.5 (g)

m : weighing out amount of sample (g)

6. Methods for Determination of Arsenic

6.1 Classification of Determination Method The method for determination of arsenic shall be in accordance with any one of the following methods.

- (1) Iron Hydroxide Coprecipitacional Separation and Arsenic Hydride Separation Silver Diethyldithiocarbamate Absorptiometry This method shall apply to the sample of 0.00005 wt% or over up to and including 0.005 wt% in arsenic content.
- (2) Iron Hydroxide and Lanthanum Hydroxide Coprecipitacional Separation Flameless Atomic Absorption Method This method shall apply to the sample of 0.00005 wt% or over up to and including 0.005 wt% in arsenic content.
- (3) Iron Hydroxide and Lanthanum hydroxide Coprecipitacional Separation Inductively Coupled Plasma Emission Spectral Method This method shall apply to the sample of 0.0001 wt% or over up to and including 0.01 wt% in arsenic content.

6.2 Iron Hydroxide Coprecipitacional Separation and Arsenic Hydride Separation Ag-DDTC Absorptiometry

6.2.1 Summary After decomposing the sample with nitric acid, add ammonium iron (III) sulfate and aqueous ammonia, and coprecipitate arsenic with iron hydroxide to be filtered. Dissolve the precipitate with sulfuric acid and with hydrochloric acid, add tin (II) chloride, potassium iodide, and sandy zinc, gasify arsenic as arsenic trihydride (hereafter, referred to as "Ag-DDTC"), make brucinechloroform solution absorb it, and measure its absorbance by using a photoelectric photometer.

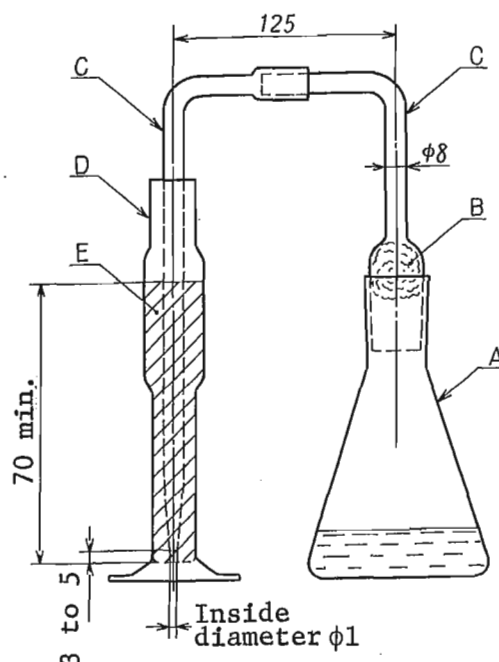
6.2.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid (1+1, 1+50)
- (2) Nitric acid (1+1)
- (3) Sulfuric acid (1+5)
- (4) Aqueous ammonia
- (5) Ammonia washing solution Add 15 g of ammonium nitrate in 500 ml of aqueous ammonia (1+5) to be dissolved.
- (6) Zinc Zinc (sandy) for arsenic analysis of JIS K 8012 [Zinc (Reagent)].
- (7) Tin (II) chloride solution Dissolve 40 g of tin (II) chloride dihydrate in 100 ml of hydrochloric acid, add small grains of metallic tin, and reserve it. Dilute only the necessary amount of this solution 10 times with water on each use.
- (8) Potassium iodide solution (200 g/l) Prepare this solution on each use.
- (9) Ammonium iron (III) sulfate solution Dissolve 5 g of ammonium iron (III) sulfate and 12 parts of water in 100 ml of nitric acid (1+100). 1 ml of this solution contains about 6 mg of iron (III).
- (10) Lead acetate solution (100 g/l) After dissolving 10 g of lead acetate trihydrate in water and 1 to 2 drops of acetic acid, make it up to 100 ml with water.
- (11) Ag-DDTC and brucine-chloroform solution Dissolve 0.25 g of Ag-DDTC and 0.05 g of brucine in 100 ml of chloroform.
- (12) Chloroform
- (13) Standard arsenic solution (1 µgAs/ml) Dissolve 0.132 g of diarsenic trioxide [JIS K 8005] in 2 ml of sodium hydroxide solution (40 g/l), dilute with water, add 1 to 2 drops of phenolphthalein solution as an indicator, and slightly acidify with sulfuric acid (1+10). After cooling to ordinary temperature, transfer this solution into a 1000 ml volumetric flask by using water, and dilute to the mark line with water to be taken as stock solution (100 µgAs/ml). Dilute only the necessary amount of this stock solution accurately 100 times with water on each use to be taken as standard arsenic solution.

6.2.3 Instruments The instruments given in Figure 5 shall be used as a rule.

Figure 5. Example of Arsenic Trihydride Generator and Absorbing Tube

Unit: mm



- A : Arsenic trihydride generating bottle 100 ml
- B : Glass fiber or chemical cotton wetted with lead acetate solution [6.2.2 (10)]
- C : Conduit
- D : Arsenic trihydride absorbing tube (with 10 ml mark line)
- E : Absorbing solution

6.2.4 Weighing out Amount of Sample The weighing out amount of sample shall be 10 g and the sample shall be weighed out to the nearest 10 mg.

6.2.5 Procedure

6.2.5.1 Preparation of Sample Solution Prepare the sample solution in accordance with the following procedure.

- (1) Weigh out a sample, and transfer it into a beaker (500 ml).
- (2) Cover with a watch glass, decompose by adding 80 ml of nitric acid (1+1), and expel nitrogen oxide by gently boiling. After cooling to ordinary temperature, wash the bottom surface of the watch glass with water, remove the watch glass, and make the amount of solution to about 200 ml by adding water (9).

Note ⁽⁹⁾ In the case where the amount of arsenic in this solution is 20 µg or over, after diluting this solution to the specific amount, take an aliquot into a beaker (500 ml) so that the amount of arsenic becomes 5 to 20 µg, and make the amount of the solution to about 200 ml by adding water.

6.2.5.2 Separation of Arsenic Separate arsenic in accordance with the following procedure.

- (1) Add 3 ml of ammonium iron (III) sulfate [6.2.2 (9)] to the solution obtained in 6.2.5.1 (2).
- (2) Add aqueous ammonia until the precipitate of copper hydroxide to be refined is dissolved with stirring this solution, and further add 50 ml excessively. Heat this solution, and gently boil for 5 minutes.
- (3) Filter the precipitate by using filter paper (class 5A), and wash several times with warm ammonia washing solution [6.2.2 (5)]. Discard both filtrate and washings.
- (4) Wash the precipitate on the filter paper into the original beaker with warm water, place the original beaker under a funnel, drop 10 ml of hydrochloric acid (1+1) onto the filter paper, dissolve the precipitate remaining on the filter paper, and wash the filter paper sufficiently with hydrochloric acid (1+50).
- (5) After dissolving the precipitate thoroughly by heating this solution, make the amount of the solution to about 200 ml by adding water. Hereafter, operate according to the procedure of (2) and (3) ⁽¹⁰⁾.
- (6) Wash the precipitate on the filter paper into the original beaker with as small amount of water as possible, place the original beaker under the funnel, drop 20 ml of warm sulfuric acid (1+5) and 2 ml of hydrochloric acid (1+1) onto the filter paper, dissolve the precipitate remaining on the filter paper, and wash the filter paper sufficiently with warm water.
- (7) After dissolving thoroughly the precipitate by heating this solution, and transfer it into a beaker (200 ml) by using a small amount of water. Further concentrate this solution by heating and make the amount of the solution to about 20 ml.
- (8) Cool this solution down to room temperature, wash into the arsenic trihydride generating bottle [6.2.3] with as small amount of water as possible, and make the amount of the solution to about 50 ml by adding water.

Note ⁽¹⁰⁾ When about 3 mg or over of copper is considered to be remaining in the precipitate, perform the procedures of (4) and (5) in 6.2.5.2.

- (9) Add 2 ml of potassium iodide solution [6.2.2 (8)] and 5 ml of tin (II) chloride solution [6.2.2 (7)], mix by shaking, and allow to stand at room temperature for about 15 minutes.

6.2.5.3 Gasification and Absorption of Arsenic Trihydride Add 5 g of sandy zinc [6.2.2 (6)] to the arsenic trihydride generating bottle of 6.2.5.2 (9), quickly connect the conduit [6.2.3] and the absorbing tube [6.2.3] containing 10 ml of Ag-DDTC and brucine-chloroform solution [6.2.2 (11)], allow to stand in water of 25°C for about an hour, and make Ag-DDTC and brucine-chloroform solution absorb arsenic trihydride.

6.2.5.4 Measurement of Absorbance Add chloroform to the absorbing solution obtained in 6.2.5.3 to make accurately 10 ml, take a portion of this solution onto the absorption cell (10 mm) of the photometer, use the Ag-DDTC and brucine-chloroform solution as contrast solution, and measure the absorbance near 510 nm in wavelength.

6.2.6 Blank Test Perform the same operation as for the sample in parallel with the sample without using the sample.

6.2.7 Preparation of Working Curve Deal out 0 to 20.0 ml of standard arsenic solution [6.2.2 (13)] (0 to 20 µg as arsenic) stepwise into several arsenic trihydride generating bottles, add 3 ml of ammonium iron (III) sulfate [6.2.2 (9)] solution, 20 ml of sulfuric acid (1+5) and 2 ml of hydrochloric acid (1+1), and make the amount of the solution to about 50 ml by adding water. Operate in parallel with the sample according to the procedures of 6.2.5.2 (9) to 6.2.5.4, prepare the relation curve between the obtained absorbance and the amount of arsenic, and transfer the relation curve in parallel so as to pass through the origin to be taken as the working curve.

6.2.8 Calculation The calculation shall be carried out in accordance with either of the following methods.

- (1) In the Case of No Aliquot in 6.2.5.1 (2) Obtain the amount of arsenic from the absorbance obtained in 6.2.5.4 and in 6.2.6 and the working curve prepared in 6.2.7, and calculate the content of arsenic in the sample by the following formula.

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

where A_1 : detected amount of arsenic in sample solution (g)

A_2 : detected amount of arsenic in blank test solution (g)

m : weighed out amount of sample (g)

- (2) In the Case of Aliquot in 6.2.5.1 (2) Obtain the amount of arsenic from the absorbance obtained in 6.2.5.4 and in 6.2.6 and the working curve prepared in 6.2.7, and calculate the content of arsenic in the sample by the following formula.

$$\text{Arsenic wt \%} = \frac{A_3 - A_4}{m \times B} \times 100$$

where A_3 : detected amount of arsenic in aliquot sample solution (g)

A_4 : detected amount of arsenic in aliquot blank test solution (g)

m : weighed out amount of sample (g)

B : aliquot ratio of sample solution and blank test solution

6.3 Iron Hydroxide and Lanthanum Hydroxide Coprecipitational Separation Flameless Atomic Absorption Method

6.3.1 Summary After decomposing a sample with nitric acid, add iron (III), lanthanum nitrate and aqueous ammonia, coprecipitate arsenic with iron hydroxide and lanthanum hydroxide, and filter. After dissolving the precipitate in nitric acid and hydrogen peroxide, inject the solution into the electrothermal furnace of a flameless absorptiometer, heat, and measure the absorbance.

6.3.2 Reagents The reagents shall be as follows.

- (1) Nitric acid (1+1, 1+50)
- (2) Nitric acid mixed solution Add 10 ml of hydrogen peroxide to 100 ml of nitric acid (1+1). Prepare this solution on each use.
- (3) Aqueous ammonia
- (4) Ammonia washing solution As described in 6.2.2 (5).
- (5) Iron (III) solution After dissolving 0.5 g of iron (99.9% or over) in 20 ml of nitric acid mixed solution [6.3.2 (2)], further heat, and expel the excessive hydrogen peroxide. After cooling to ordinary temperature, dilute to 100 ml with water. 1 ml of this solution contains about 5 mg of iron (III).
- (6) Lanthanum nitrate solution Dissolve 1.6 g of lanthanum nitrate hexahydrate in 100 ml of nitric acid (1+100). 1 ml of this solution contains about 5 mg of lanthanum.
- (7) Standard arsenic solution (2 µgAs/ml) Dilute only a necessary amount of stock solution (100 µgAs/ml) prepared in 6.2.2 (13) accurately 50 times with water on each use to be taken as the standard arsenic solution.

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6.3.3 Weighing out Amount of Sample Weigh out a sample by 10 g to the nearest 10 mg.

6.3.4 Procedure

6.3.4.1 Preparation of Sample Solution Prepare the sample solution in accordance with the following procedure.

- (1) Weigh out a sample, and transfer into a beaker (500 ml).
- (2) Cover with a watch glass, decompose by adding 80 ml of nitric acid (1+1), and expel nitrogen oxide by gently boiling. After cooling to room temperature, wash the under surface of the watch glass with water, remove the watch glass, and make the amount of solution to about 200 ml by adding water.

6.3.4.2 Separation of Arsenic Separate arsenic in accordance with the following procedure.

- (1) Add 4 ml of iron (III) solution [6.3.2 (5)] and 4 ml of lanthanum nitrate solution [6.3.2 (6)] to the solution obtained in 6.3.4.1 (2), add aqueous ammonia with stirring this solution until the precipitate of copper hydroxide to be refined is dissolved, and further add 50 ml in excess. Heat this solution and gently boil for 5 minutes.
- (2) Filter the precipitate by using filter paper (class 5B), and wash several times with warm ammonia washing solution [6.3.2 (4)]. Discard filtrate and washings.
- (3) Transfer the precipitate on the filter paper into the original beaker by washing with warm water, place the original beaker under a funnel, drop 10 ml of nitric acid mixed solution [6.3.2 (2)] onto the filter paper, dissolve the remaining precipitate on the filter paper, and wash the filter paper sufficiently with warm nitric acid (1+50).
- (4) Heat filtrate and washings, dissolve thoroughly the precipitate, and besides expel the excessive hydrogen peroxide. After cooling to ordinary temperature, transfer into a 100 ml volumetric flask by using water, and dilute to the mark line with water ⁽¹¹⁾.

Note ⁽¹¹⁾ In the case where the amount of arsenic in this solution is 10 µg or over, take an aliquot into a 100 ml volumetric flask so that the amount of arsenic becomes 5 to 10 µg. Add iron (III) [6.3.2 (5)] solution and lanthanum nitrate solution [6.3.2 (6)] solution so that the amount of iron and the amount of lanthanum in this aliquot solution become respectively 20 mg, and further add nitric acid (1+1) so that the amount of nitric acid becomes 5 ml, thereafter dilute it with water to the mark line.

6.3.4.3 Measurement of Absorbance Inject the specific amount (¹²) of the solution obtained in 6.3.4.2 (4) into the electrothermal furnace of a flameless atomic absorptiometer, heat, and measure the absorbance (¹³) at 193.7 nm in wavelength.

Notes (¹²) Though 10 or 20 µl is generally injected, the amount of injection shall be determined by conforming to the measuring range of each apparatus.

(¹³) Measurement may be performed by using the scale or the like of an indicator proportional to the absorbance.

6.3.5 Blank Test Perform the same procedure as for the sample concurrently with the sample without using the sample.

6.3.6 Preparation of Working Curve Prepare the working curve in accordance with the following procedure.

- (1) Take 4 ml of iron (III) solution [6.3.2 (5)] and 4 ml of lathanum nitrate solution [6.3.2 (6)] into several 100 ml volumetric flasks, and add 10 ml of nitric acid (1+1).
- (2) Add stepwise 0 to 5.0 ml of standard arsenic solution [6.3.2 (7)] (0 to 10 µg as arsenic), and dilute to the mark line with water.
- (3) Inject the specific amount of the obtained solution into the electrothermal furnace of a flameless atomic absorptiometer, heat, measure the absorbance at 193.7 nm in wavelength concurrently with the sample, prepare the relation curve between the obtained absorbance and the amount of arsenic, transfer the relation curve in parallel so as to pass through the origin, and take it as the working curve.

6.3.7 Calculation The calculation shall be carried out in accordance with either of the following cases.

- (1) In the Case of No Aliquot in 6.3.4.2 (4) The amount of arsenic shall be obtained from the absorbance obtained in 6.3.4.3 and in 6.3.5 and the working curve prepared in 6.3.6, and the content of arsenic in the sample shall be calculated from the following formula.

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

where A_1 : detected amount of arsenic in sample solution (g)

A_2 : detected amount of arsenic in blank test solution (g)

m : weighed out amount of sample (g)

- (2) In the Case of Aliquot in 6.3.4.2 (4) The amount of arsenic shall be obtained from both the absorbance obtained in 6.3.4.3 and in 6.3.5 and the working curve prepared in 6.3.6, and the content of arsenic in the sample shall be calculated from the following formula.

$$\text{Arsenic wt \%} = \frac{A_3 - A_4}{m \times B} \times 100$$

where A_3 : detected amount of arsenic in aliquot sample solution (g)

A_4 : detected amount of arsenic in aliquot blank test solution (g)

m : weighed out amount of sample (g)

B : aliquot ratio of sample solution and blank test solution

6.4 Iron Hydroxide and Lanthanum Hydroxide Coprecipitational Separation Inductively Coupled Plasma Emission Spectral Method

6.4.1 Summary After decomposing a sample with nitric acid, add iron (III), lanthanum nitrate and aqueous ammonia, coprecipitate arsenic with iron hydroxide and lanthanum hydroxide, and filter. After dissolving the precipitate in nitric acid and hydrogen peroxide, spray the solution into the argon plasma of an inductively coupled plasma emission spectral apparatus, and measure the emission intensity.

6.4.2 Reagents The reagents shall be as follows,

- (1) Nitric acid (1+1, 1+50)
- (2) Nitric acid mixed solution As described in 6.3.2 (2).
- (3) Aqueous ammonia
- (4) Ammonia washing solution As described in 6.2.2 (5).
- (5) Iron (III) solution As described in 6.3.2 (5).
- (6) Lanthanum nitrate solution As described in 6.3.2 (6).
- (7) Standard arsenic solution (50 µgAs/ml) Dilute only a necessary amount of the stock solution (100 µgAs/ml) prepared in 6.2.2 (13) accurately two times with water on each use to be taken as the standard arsenic solution.

6.4.3 Weighing out Amount of Sample Weigh out 20 g of a sample to the nearest 10 mg.

6.4.4 Procedure

6.4.4.1 Preparation of Sample Solution Prepare the sample solution in accordance with the following procedure.

- (1) Weigh out the sample and transfer it into a beaker (500 ml).
- (2) Cover with a watch glass, decompose by adding 160 ml of nitric acid (1+1), and expel nitrogen oxide by gently boiling. After cooling to room temperature, wash the bottom surface of the watch glass with water, remove the watch glass, and make the amount of the solution to about 200 ml by adding water.

6.4.4.2 Separation of Arsenic Separate arsenic in accordance with the following procedure.

- (1) Add 4 ml of iron (III) solution [6.4.2 (5)] and 4 ml of lanthanum nitrate solution [6.4.2 (6)] to the solution obtained in 6.4.4.1 (2), add aqueous ammonia with stirring this solution until the precipitate of copper hydroxide to be refined is dissolved, and further add 50 ml in excess. Heat this solution and gently boil for 5 minutes.
- (2) Filter the precipitate by using filter paper (class 5 B), and wash several times with warm ammonia washing solution [6.4.2 (4)]. Discard filtrate and washings.
- (3) Transfer the precipitate on the filter paper into the original beaker by washing with warm water, place the original beaker under a funnel, drop 10 ml of nitric acid mixed solution [6.4.2 (2)] onto the filter paper, dissolve the remaining precipitate on the filter paper, and wash the filter paper thoroughly with warm nitric acid (1+50).
- (4) Heat filtrate and washings. After dissolving the precipitate thoroughly, transfer into a beaker (200 ml) by using a small amount of water, and concentrate this solution by heating to make the amount of the solution to about 10 ml. After cooling to ordinary temperature, transfer into a 25 ml volumetric flask by using water, and dilute to the mark line with water (¹⁴).

Note (¹⁴) In the case where the amount of arsine is 250 µg or over in this solution, an aliquot shall be taken into a 25 ml volumetric flask so that the amount of arsine becomes 20 to 250 µg. So that the amount of iron and the amount of lanthanum become respectively 20 mg in this aliquot solution, iron (III) solution and lanthanum nitrate solution shall be added. Further, after adding nitric acid (1+1) so that the amount of nitric acid becomes 5 ml, dilute it with water up to the mark line.

6.4.4.3 Measurement of Emission Intensity Spray a portion of the solution obtained in 6.4.4.2 (4) into the argon plasma of the inductively coupled plasma emission spectral apparatus and measure the emission intensity at 193.696 nm in wavelength ⁽¹⁵⁾.

Note ⁽¹⁵⁾ In the case where precision and accuracy have been confirmed, the measurement may be performed by using another wavelength. For an apparatus capable of using the higher-order of spectral line, the higher-order of spectral line may be used, and further for an apparatus attached with a background correcting mechanism, the background correcting mechanism may be used.

6.4.5 Blank Test Perform the same procedure as for the sample concurrently the sample without using the sample.

6.4.6 Preparation of Working Curve Prepare the working curve in accordance with the following procedure.

- (1) Take 4 ml of iron (III) solution [6.4.2 (5)] and 4 ml of lanthanum nitrate solution [6.4.2 (6)] into several 25 ml volumetric flasks, and add 10 ml of nitric acid (1+1).
- (2) Add stepwise 0 to 5.0 ml of standard arsenic solution [6.4.2 (7)] (0 to 250 µg as arsenic), and dilute with water up to the mark line.
- (3) Spray a portion of the obtained solution into the argon plasma of the inductively coupled plasma emission spectral apparatus, measure the emission intensity at 193.696 nm in wavelength concurrently with the sample ⁽²⁾, prepare the relation curve between the obtained emission intensity and the amount of arsenic, transfer the relation curve in parallel so as to pass through the origin to be taken as the working curve.

6.4.7 Calculation The calculation shall be in accordance with either of the following cases.

- (1) In the Case of No Aliquot in 6.4.4.2 (4) Obtain the amount of arsenic from both the emission intensity obtained in 6.4.4.3 and in 6.4.5 and the working curve prepared in 6.4.6, and calculate the content of arsenic in the sample from the following formula.

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

where A_1 : detected amount of arsenic in sample solution (g)

A_2 : detected amount of arsenic in blank test solution (g)

m : weighed out amount of sample (g)