

JIS

JAPANESE INDUSTRIAL STANDARD

Methods for Chemical Analysis
of Nickel-Chromium-Iron Alloys

JIS G 1281-1977
(Reaffirmed: 1983)

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JAPANESE INDUSTRIAL STANDARD

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Methods for Chemical Analysis of
Nickel-Chromium-Iron AlloysG 1281-1977
(Reaffirmed: 1983)1. Scope

This Japanese Industrial Standard specifies the methods for chemical analysis of chemical components (carbon, silicon, manganese, phosphorus, sulfur, nickel, chromium, iron, copper, aluminium, titanium and cobalt) of nickel-chromium-iron alloys specified as follows:

JIS G 4901
JIS G 4902
JIS G 4903
JIS G 4904

2. General Matters

General matters common to the chemical analysis methods shall be in accordance with JIS K 0050 and JIS K 0115.

3. Method for Determination of Carbon

3.1 Classification of Methods The method for determination of carbon shall be in accordance with either one of the following methods:

- (1) Gas Volumetric Method This method applies to the sample of not less than 0.05 % in carbon content.
- (2) Electric Conductivity Method This method applies to the whole range of carbon content.
- (3) Coulometric Method This method applies to the whole range of carbon content.

3.2 Gas Volumetric Method

3.2.1 Summary A sample is ignited in a current of oxygen and carbon is completely oxidized to carbon dioxide. It is collected into a burette together with oxygen and the volume of total gas is measured. Then, after removing carbon dioxide by absorption, the volume of residual gas is measured and the loss of volume is obtained.

3.2.2 Reagents The reagents shall be as follows:

- (1) Oxygen Oxygen of not less than 99.5 v/v %
- (2) Ignition Improver The copper, tin, iron and chromium oxide by the use of 1 g respectively of which the increase of the blank test value is of not more than 0.2 ml as carbon dioxide. One kind or two kinds thereof are used.

Applicable Standards: See page 60.

3.2.3 Apparatus and Device The following apparatus and devices shall, as a rule, be used (refer to Attached Fig. 1).

- (1) Oxygen Cleaner For the purposes of removing carbon dioxide or organic gases, etc. contained in oxygen to be used and of cleanly drying oxygen, this cleaner shall be assembled by the successive connection⁽²⁾ of the washing bottle (c) put with chromic acid saturated sulfuric acid⁽¹⁾, the tube or tower (d) packed with soda lime, soda asbestos or sodium hydroxide and the washing bottle or tower (e) put with sulfuric acid or active alumina.
- (2) Combustion Furnace The combustion furnace shall be assembled by inserting⁽³⁾ the porcelain combustion tube (CT 2)(h) of 20 or 24 mm in inside diameter having a length capable of respectively being projected by each about 200 mm from both ends of the tubular electric furnace (g) into the tubular electric furnace of about 30 mm in inside diameter and 200 to 300 mm in length and the temperature⁽⁴⁾ just above the combustion tube at the central part of the furnace shall be able to be measured with a thermoelectric thermometer (i). The tubular electric furnace shall be able to control temperature by adjusting electric current, to keep a fixed temperature for a length of about not shorter than 150 mm at the central part of the furnace and be commonly used at 1450°C. The porcelain combustion tube is packed with asbestos covering over about 50 mm at the rear of the central part to be inserted with a porcelain combustion boat. Instead of the tubular electric furnace, a high frequency induction heating furnace (Attached Fig. 2) may be used.
- (3) Gas Analyzer The gas analyzer shall be assembled by successive connection of the followings:
 - (a) Sulfur dioxide absorption bottle (j) It is put with about 5 ml of the solution which is acidified by adding 1 ml sulfuric acid (1+1) to 10 ml potassium permanganate solution⁽⁵⁾ (5 w/v %). Otherwise, manganese dioxide may be used.
 - (b) Cooling tube (k)
 - (c) Three-way stopcock (l) One way is kept open to the open air.
 - (d) Three-way stopcock (m)
 - (e) Burette (n) The burette is put with sodium chloride solution (26 w/v %) which is slightly acidified⁽⁶⁾ by dropping sulfuric acid until it finally turns red after adding Methyl Red solution, which is made to be of about 350 ml in total capacity, 50 ml in graduated portion and 0.1 ml in notched scale unit. However, this scale shall be notched by taking 16°C and 760 mm Hg as standard state.
 - (f) Leveling bottle (o)
 - (g) Carbon dioxide absorption bottle (p) It is put with potassium hydroxide solution (33 w/v %).

(h) Thermometer (q) It is equipped for measuring the temperature of gas in a burette. It shall be able to read out to 0.10°C.

- (4) Porcelain Combustion Boat and Porcelain Combustion Boat Cover
The porcelain combustion boat (CB 1 or CB 2) shall be preliminarily, in blank, burnt at a using combustion temperature in oxygen current to be used. The porcelain combustion boat cover (CBC 1) may be used jointly with the porcelain combustion boat. The porcelain combustion boat cover shall be preliminarily, in blank, burnt in the same way as that for porcelain combustion boat to be used.

3.2.4 Weighing Out Amount of Sample and Additional Amount of Ignition Improver The weighing out amount of sample and the additional amount of ignition improvers shall be as specified in Table 1.

Table 1

Carbon content %	Weighing out amount of sample g	Additional amount of ignition improver g		
		Tin	Copper	Iron
0.05 and over, up to 0.3	2.0	10	1.0	1.0

3.2.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Connect the apparatus of 3.2.3, raise the temperature in a combustion tube to 1300 to 1400°C, confirm the airtightness of the apparatus⁽⁷⁾ and close three-way stopcocks (l) and (m).
- (2) Then, open the oxygen inlet part of combustion tube, insert the porcelain combustion boat put with a sample⁽⁸⁾ into the central part of the combustion tube and immediately airtightly stopper it. Thereafter, open a cock (f) and let it stand for about 2 min with feeding oxygen. Thereafter, place a leveling bottle (o) at the position of the bulb part of a burette (n), open the three-way stopcocks (l) and (m) to the furnace side, conduct the mixed gas of carbon dioxide and oxygen into the burette (n) through a sulfur dioxide absorption bottle (j)⁽⁹⁾ and a cooling tube (k) with regulating the three-way stopcock (l) or (m) and complete the combustion of the sample in about one half the bulb part of the burette (n). Then, place the leveling bottle (o) at a position lower than the bottom part scale of burette (n) and collect the mixed gas to near the bottom part of the scale of burette (n) in about 30 sec. Thereafter, close the three-way stopcocks (l) and (m), stop the supply of oxygen by closing the cock (f) and let it stand for about 1 min.

- (3) Then, vertically move the leveling bottle (o) along the burette (n), coincide the levels of the solutions in the burette (n) and the leveling bottle (o) to each other, read the scale of burette (n) and allow it to be the volume of mixed gas.

Further, measure the temperature of the mixed gas at that time with a thermometer (q)⁽¹⁰⁾.

- (4) Then, open the three-way stopcock (m) to the carbon dioxide absorption bottle (p) side, raise the leveling bottle (o) to a position exceeding that of the burette (n), fill solution into the inside of burette (n), feed mixed gas into the carbon dioxide absorption bottle (p), let carbon dioxide be absorbed into potassium hydroxide solution, then lower the leveling bottle (o) to a position lower than that of the bottom part scale of burette (n), return residual gas to the burette (n) and close the three-way stopcock (m). After letting it stand for about 1 min, coincide the levels of the solutions in the burette (n) and the leveling bottle (o) to each other by moving the leveling bottle (o), read the scale of the burette (n) and allow it to be the volume of residual gas.

Further, measure the temperature of residual gas at that time with the thermometer (q)⁽¹⁰⁾.

- (5) Repeat the operation of (4) and confirm that there has been no change in the volume of residual gas. Thereafter, open the three-way stopcock (l) to the open air side, raise the leveling bottle (o) to a position exceeding that of burette (n), discharge residual gas and close the three-way stopcocks (l) and (m)⁽¹¹⁾.

3.2.6 Calculation Subtract the volume of residual gas from the volume of mixed gas, obtain the volume of carbon dioxide by the sample and calculate the content of carbon in the sample⁽¹³⁾ from the following formula by utilizing the correction coefficient (f)⁽¹²⁾ of Attached Table 1.

$$\text{Carbon (\%)} = \frac{A \times 0.0005027}{W} \times f \times 100$$

where

A: volume of carbon dioxide (ml)

W: weighing out amount of sample (g)

f: correction coefficient (Attached Table 1)

Notes (1) When chromic acid saturated sulfuric acid turns green, the oxidizing force is lost. Therefore, it shall be renewed.

(2) Because there is a fear that a rubber tube absorbs carbon dioxide, both ends of each connection of the apparatus shall be brought into close relation by using a glass tube and shall be necessarily kept with a rubber tube or a vinyl tube.

- (3) For the rubber stoppers of the connection parts of the porcelain combustion tube of combustion furnace to the oxygen cleaner and the gas absorber, the silicone rubber having great heating resistance should preferably be used.
- (4) The difference between the indication temperature of a thermoelectric thermometer and the temperature in a combustion tube shall be carefully and necessarily corrected.
- (5) Instead of potassium permanganate solution, chromic anhydride solution (50 w/v %) may be used.
- (6) Instead of sodium chloride solution (26 w/v %), dilute sulfuric acid may be used. For the dilute sulfuric acid in that case, water is added with Methyl Red solution and slightly acidified by dropping sulfuric acid until it just turns red.
- (7) The airtightness test shall be carried out as follows: Close a cock (f), place a leveling bottle (o) at a position lower than that of the lower part scale of burette (n) and open three-way stopcocks (l) and (m) to the furnace side. Then, gradually open the cock (f), collect oxygen to a position of 10 to 20 ml of the scaled part in burette (n), close the cock (f), let it stand for a while and confirm no change in the surface of solution in burette (n). If the surface of solution is likely to fall, it indicates the presence of bad airtightness between the cock (f) and the burette (n). Then, open the three-way stopcock (m) to the furnace side and the three-way stopcock (l) to the open air side, raise the leveling bottle (o) to a position exceeding that of burette (n), discharge the oxygen in burette (n) to the open air and close the three-way stopcocks (l) and (m).
- (8) When the adhesion of oils to a sample is observed, it shall be cleaned with ethyl alcohol and ethyl ether and used after drying. When the sample is prepared, cases shall be taken so that it does not become a too small sample or a long winding sample. Further, when the sample is handled, it shall be handled with a pincette or a metal spoon so that it is not stained with hand or the like and stored in a clean glass bottle.
- (9) When the turbidity of the solution in this absorption bottle (j) is observed, it shall be replaced by new one.

In the case where chromic anhydride solution is used instead of potassium permanganate solution, if the solution turns bluish, it shall be replaced by new one. Further, because carbon dioxide sometimes remains in a sulfur dioxide absorption bottle (j), cares shall be necessarily taken therefore.

- (¹⁰) There shall be no difference between the temperature of mixed gas and the temperature of residual gas. When the temperatures of the solution in burette and the solution in carbon dioxide absorption bottle are low in winter, to prevent the generation of temperature difference, the blank passing of oxygen or the test by standard sample shall be preliminarily necessarily carried out.
- (¹¹) To make sure once more, collect the gas in combustion tube with a burette, analyze it and confirm the absence of residual carbon dioxide. Thereafter, remove the stopper of combustion tube and take out the porcelain combustion boat. After cooling the taken out porcelain combustion boat, the fusion state and the oxidation state of the sample shall be necessarily examined.
- (¹²) In the case where dilute sulfuric acid is used instead of sodium chloride solution (26 w/v %), the correction coefficient (f') of Attached Table 2 shall be used. The calculation formula of the carbon content in that case shall be as follows:

$$\text{Carbon (\%)} = \frac{A \times 0.0005005}{W} \times f' \times 100$$

where A : volume of carbon dioxide (ml)

 W : weighing out amount of sample (g)

 f' : correction coefficient (Attached Table 2)

- (¹³) A blank test shall be carried out by using the porcelain combustion boat into which the same amount of ignition improvers as those added to the sample are weighed out.

In daily operation, at the initial, middle and final periods of operation time, the analysis shall be necessarily carried out by using the sample having a known carbon content and the conditions of the apparatus or the like in that day shall be examined.

Remark: The operation in the case where a high frequency induction heater is used, shall be as follows:

Connect the apparatus of Attached Fig. 2 and confirm its airtightness. Thereafter(¹⁴), close a three-way stopcock (m) and let a three-way stopcock (l) be open to the open air.

Then, insert the crucible put with a sample(¹⁵) and ignition improver(¹⁵) into a combustion cylinder, tightly stopper it, feed oxygen by wholly opening an oxygen switching valve (F) and a flow rate regulation valve (E) and expel the air in combustion cylinder. Thereafter, close the three-way stopcock (l) and turn on a high frequency switch (C).

After 10 to 20 sec have elapsed, open the three-way stopcock (m) to the furnace side, further slightly open the three-way stopcock (l) to the furnace side, gradually conduct mixed gas into a burette(n) through a sulfur dioxide absorption bottle (j)⁽⁹⁾ and a cooling tube (k), allow about 1 min to have elapsed and after the combustion of sample has been almost ended, quickly collect the mixed gas to near the bottom part of the scale of burette (n). Thereafter, close the three-way stopcocks (l) and (m), disconnect high frequency current by turning on a high frequency disconnecting switch (I), stop the feed of oxygen and let it stand for about 1 min. Hereafter, determine carbon in accordance with the procedures on and after 3.2.5 (3).

- Notes ⁽¹⁴⁾ Before the determination, the airtightness test shall be necessarily carried out and cares shall be taken for the airtightness. The airtightness test shall be carried out in accordance with Note ⁽⁷⁾, as appropriate.
- ⁽¹⁵⁾ The sample and the ignition improver shall, as a rule, be weighed out in accordance with Table 2. However, each blank test value of ignition improver shall be necessarily under 0.2 ml as carbon dioxide amount per 1 g thereof. Further, the chromium oxide powder herein is preliminarily heated at about not lower than 1300°C in a current of oxygen for about not less than 1 h and carbon is removed. Thereafter, it is cooled and pulverized to not more than 149 µm (100 mesh). It shall be sufficiently incorporated with the sample and used. Further, it may be added with iron, as required.

Table 2

Carbon content %	Weighing out amount of sample g	Additional amount of ignition improver g	
		Tin	Chromium oxide powder
0.05 and over, up to 0.3	1.5	0.5	About 0.05

3.3 Electric Conductivity Method

3.3.1 Summary A sample is ignited in a current of oxygen and carbon is completely oxidized to carbon dioxide. It is absorbed with a fixed amount of alkali solution and the variation of the electric conductivity of the alkali solution before and after absorbing carbon dioxide is measured.

3.3.2 Reagents The reagents shall be as follows:

- (1) Alkali Solution Sodium hydroxide, potassium hydroxide or barium hydroxide solution of a suitable concentration of N/10 to N/200 level is prepared according to the using apparatus.

That is, by using the pure water from which carbon dioxide is removed, 1N alkali solution is prepared to be the stock solution. Then, by using the pure water from which carbon dioxide is removed by passing the air or oxygen for a long time from which carbon dioxide is removed, the stock solution is diluted and alkali solution of a specified concentration is prepared. It is transferred into the polyethylene vessel attached with the carbon dioxide absorption tube packed with soda lime or sodium hydroxide, to be stored and taken out by using an automatic burette or the like.

- (2) Oxygen Oxygen of not less than 99.5 v/v %
- (3) Ignition Improver Any one of copper, tin, iron and chromium oxide shall be as little in carbon content as possible.

3.3.3 Apparatus and Devices The following apparatus and devices shall, as a rule, be used (refer to Attached Fig. 3).

- (1) Oxygen Cleaner It shall be assembled in accordance with the oxygen cleaner of 3.2.3 (1), or otherwise by the successive connection of the tube packed with granular copper oxide heated at 800 to 850°C, an empty bottle and the washing bottle put with chromic acid saturated sulfuric acid⁽¹⁾ and the tube or tower packed with soda lime or sodium hydroxide. However, pure oxygen shall be used and when the necessity for using a copper oxide tube is not considered, it may be omitted.

Further, the oxygen discharge bottle for regulating the flow rate of oxygen gas may be established to the rear of the tube or tower packed with soda lime or sodium hydroxide.

- (2) Combustion Furnace It shall be in accordance with the combustion furnace of 3.2.3 (2) as appropriate. However, in the case where asbestos is not packed into a combustion tube, the iron oxide powder collection tube packed with asbestos or quartz wool shall be connected to the rear of the combustion tube.

Further, if excess oxygen is discharged from the sample induction port of combustion tube to prevent the intrusion of air into the tube, the sample induction port may be open. Instead of a tubular electric furnace, a high frequency induction heater (refer to Attached Fig. 2) may be used.

- (3) Sulfur Dioxide Remover It shall be assembled by connecting the sulfur dioxide absorption bottle of 3.2.3 (3)(a) or the tube packed with manganese dioxide to the rear of the combustion tube.
- (4) Electric Conductivity Measuring Apparatus For the purpose of absorption of carbon dioxide discharged from combustion tube, the electrode for measuring electric conductivity is respectively enclosed in each of the coiled state absorption tube put with a fixed amount of alkali solution and of the coiled state absorption tube put with a fixed amount of alkali solution for reference standard, and they are put into the thermostatic bath capable of keeping at a fixed temperature to form the main

body. The quantitative pump or vacuum pump for feeding combustion gas into the absorption tubes at a fixed flow rate, a gas reservoir and a flowmeter are mounted to the front or rear of the carbon dioxide absorption coiled tube.

- (5) Recorder The signal is taken out as the electric conductivity changed amount obtained by a Wheatstone bridge and let indicate a value corresponding to the analytical component content with an automatic balance carried out recorder or the like.

Further, this indication may be carried out in accordance with either the record by a recording paper or the direct reading on a scale.

- (6) Porcelain Combustion Boat and Porcelain Combustion Boat Cover
The porcelain combustion boat and the porcelain combustion boat cover shall be in accordance with 3.2.3 (4), as appropriate. However, in the case where many boats are, in blank, burnt at a time, after cooling, they are taken out with a pincette and stored in the desiccator not coated with grease or the like. The use of the boat having a high blank test value because of the storage for a long time shall be avoided and they shall be, in blank, burnt again.

3.3.4 Weighing Out Amount of Sample and Additional Amount of Ignition Improvers An amount most suitable for the using apparatus of a sample shall be weighed out and its amount shall be confirmed by analysis of the standard sample having a known carbon content. Copper, tin and iron shall be added to the sample as ignition improver⁽²⁾. The additional amount of ignition improvers shall be 0.5 to 1.0 g per 1 g of the sample and one or two kinds thereof shall be added.

3.3.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Raise the temperature in a combustion tube to 1300 to 1400°C and keep the thermostatic bath of an electric conductivity measuring apparatus at a fixed temperature. Then, turn on the switch of a pump and pass oxygen through the apparatus. Put a fixed amount of alkali solution into the absorption tube for measurement of electric conductivity, pass oxygen and regulate the zero point of the recorder for measurement of electric conductivity.
- (2) Then, insert the porcelain combustion boat in which a sample⁽³⁾ is weighed out into the central part of the combustion tube and successively feed oxygen. When the sample burns and carbon dioxide starts to be absorbed with alkali solution, allow the pointer of a recorder to start to be moved and determine carbon⁽⁵⁾ from the indicated value⁽⁴⁾ when the pointer is stabilized.

Notes (1) The chromic acid saturated sulfuric acid herein shall be in accordance with 3.2 Note (1), as appropriate.

- (2) In the case where a high frequency induction heater is used, tin and chromium oxide powder shall be used as ignition improvers. The additional amount thereof shall be in accordance with 3.2 Note ⁽¹⁵⁾, as appropriate.
- (3) The sample herein shall be in accordance with 3.2 Note ⁽⁸⁾, as appropriate.
- (4) Standard sample having a known carbon content shall be preliminarily analyzed in the same operation and no difference between the indication value of recorder and the standard value shall be confirmed. If there is some difference, the difference shall be removed by regulation of the sensitivity of recorder.
- (5) The complete oxidation of sample shall be confirmed and the test of the apparatus by using standard sample and the blank test shall be respectively in accordance with 3.2 Note ⁽¹³⁾, as appropriate.

3.4 Coulometric Method

3.4.1 Summary A sample is ignited in a current of oxygen and carbon is completely oxidized to carbon dioxide. It is absorbed with the barium perchlorate solution preliminarily established at a fixed pH value. The quantity of electricity consumed for preparing equivalent alkali necessary for neutralizing the amount of increased hydrogen ion at that time by electrolysis, is measured.

3.4.2 Reagents The reagents shall be as follows:

- (1) Barium Perchlorate Absorption Solution The barium perchlorate absorption solution of a suitable concentration is prepared according to the using apparatus. Generally, 25 g barium perchlorate is dissolved with about 100 ml water, added with 10 to 15 ml isopropyl alcohol and diluted to 500 ml with water to be used.
- (2) Barium Perchlorate Electrolyte The barium perchlorate electrolyte of a suitable concentration is prepared according to the using apparatus. Generally, 15 to 20 g barium perchlorate is dissolved with water and diluted to 100 ml with water to be used.
- (3) Reference Electrode Vessel Solution A suitable solution is used according to the using apparatus. Generally, 25 g barium perchlorate and 10 to 20 g sodium chloride are dissolved with about 200 ml water, added with 10 to 15 ml isopropyl alcohol and diluted to 500 ml with water to be used.
- (4) Barium Carbonate
- (5) Oxygen The oxygen of not less than 99.5 v/v %.
- (6) Ignition Improvers Any one of tin, iron and chromium oxide shall be as little in carbon content as possible.

3.4.3 Apparatus and Devices The following apparatus and devices shall, as a rule, be used (refer to Attached Fig. 4)

- (1) Oxygen Cleaner For the purposes of removing carbon dioxide or organic gases, etc. contained in oxygen to be used and of cleanly drying oxygen, it shall be assembled by connecting the small electric furnace to heat the tube packed with platinum asbestos, granular copper oxide, etc. at about 800°C to the tube or tower packed with soda lime or sodium hydroxide, or otherwise shall be in accordance with the oxygen cleaner of 3.2.3 (1), as appropriate.
- (2) Oxygen Pressure Regulator For the purpose of avoiding the incomplete combustion of a sample due to the shortage of oxygen, the oxygen pressure regulator shall always keep the pressure of oxygen in a combustion tube constant.
- (3) Combustion Furnace It shall be in accordance with 3.2.3 (2) and 3.3.3 (2), as appropriate.
- (4) Sulfur Dioxide Remover It shall be in accordance with 3.3.3 (3), as appropriate.
- (5) Combustion Gas Flow Divider In the case where the carbon content of sample is much, and in the case of quick analyzation and in other cases the combustion gas flow divider shall be able to divide the flow of a fixed amount from the combustion gas exhausted from a combustion tube⁽¹⁾.
- (6) Carbon Dioxide Absorption Vessel and Coulometric Titration Vessel The cathodic vessel put with an almost fixed amount of barium perchlorate absorption solution⁽²⁾ for absorbing carbon dioxide exhausted from a combustion tube and the anodic vessel put with an almost fixed amount⁽⁴⁾ of barium carbonate⁽³⁾ and barium perchlorate electrolyte are united by the partition of porous diaphragm and the platinum electrodes⁽⁵⁾ for coulometric titration shall be inserted into both vessels. Further, for the purpose of measuring pH of cathodic vessel absorption solution, the reference electrode vessel put with reference electrode vessel solution is united with the cathodic vessel by the partition of porous diaphragm, a glass electrode shall be inserted into the cathodic vessel and a reference electrode⁽⁶⁾ into the reference electrode vessel.

Further, the cathodic vessel should preferably be so constructed thha the surface of absorption solution can be sealed with purified oxygen or the like so that the absorption solution does not absorb the carbon dioxide in the open air during analytical operation.

- (7) Instrumentation Equipments The instrumentation equipment shall be equipped with a pH detection amplifier circuit, an electrolytic signal generation circuit, a control circuit and an indicating circuit.

- (a) pH Detection Amplifier Circuit It shall be composed of the detection part consisting of a glass electrode and a reference electrode [inserted into the carbon dioxide absorption vessel and coulometric titration vessel of 3.4.3 (6)] and the amplifier part.
 - (b) Electrolytic Signal Generation Circuit It is the circuit generating a fixed quantity of current for electrolysis and shall be able to accurately measure the quantity of electricity required for electrolysis.
 - (c) Control Circuit It is the circuit controlling electrolysis. When pH of cathodic absorption solution moves to a more acid side than a setting value, the electrolytic amount increases in proportion to the amount of movement. When pH approaches the setting value, the electrolytic amount decreases. When pH coincides with the setting value, the control circuit shall operate not to carry out electrolysis.
 - (d) Indication Circuit It is the circuit indicating the quantity of electricity required for electrolysis as the result of analysis. It should preferably indicate digital amount by four figures at least by using an electromagnetic counter or the like. Further, it should preferably be so designed that the quantity of electricity of one count of the indication corresponds to 8×10^{-3} coulomb, that is, 0.5×10^{-6} g in carbon amount.
- (8) Porcelain Combustion Boat and Porcelain Combustion Boat Cover
The porcelain combustion boat and the porcelain combustion boat cover shall be in accordance with 3.2.3 (4) and 3.3.3 (6), as appropriate.

3.4.4 Weighing Out Amount of Sample and Additional Amount of Ignition Improves For the sample, an amount most suitable for the apparatus to be used shall be weighed out and its amount shall be confirmed by analysis of the standard sample having a known carbon content⁽⁷⁾. Copper, tin and iron shall be added to the sample as ignition improvers⁽⁸⁾. The additional amount of ignition improvers shall be of 0.5 to 1.0 g per 1 g of the sample and one or two kinds thereof shall be added.

3.4.5 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Raise the temperature in a combustion tube to 1300 to 1400°C, respectively put almost fixed amount of barium perchlorate absorption solution⁽²⁾ into the cathodic vessel of coulometric titration vessel, almost fixed amount⁽⁴⁾ of barium carbonate⁽³⁾ and barium perchlorate electrolyte into the anodic vessel, and a required amount of reference electrode vessel solution into the reference electrode vessel and pass oxygen through the apparatus. Establish pH of barium perchlorate absorption solution of cathodic vessel at a fixed value between 9 to 10.4 by electrolysis and regulate various conditions of gas flow divider and instrumentation equipments.

- (2) Then, open the oxygen inlet part of combustion tube, insert the porcelain combustion boat in which a sample⁽⁹⁾ is weighed out, into the central part of combustion tube and immediately airtightly stopper it. When the sample burns and carbon dioxide starts to be absorbed with barium perchlorate absorption solution, allow the counter of indication circuit to start to move. Allow it to become gradually slower at near the end point and to become finally in a stop state. Allow the point where this stop state is reached, to be the end point, read the number of counts and obtain the content of carbon⁽¹⁰⁾⁽¹¹⁾.

Notes (1) The flow divider should preferably be able to make the flow dividing ratio be accurately of 1 to 1, 1 to 9, 1 to 24, 1 to 49 etc.

(2) When contaminated, the barium perchlorate absorption solution shall be replaced.

(3) Barium carbonate shall be added until the diaphragm disappears from sight. When barium carbonate decreases after use for a long time, the decreased amount shall be added.

(4) Barium perchlorate electrolyte shall be added to 10 mm above the platinum electrode.

(5) The size of platinum electrode should preferably be not less than 2 mm² at least.

(6) A silver-silver chloride electrode shall, as a rule, be used for the reference electrode.

(7) For the weighing out amount of sample, 1.0 to 0.10 g shall, as a rule, be used according to the carbon content.

Further, when the carbon content is high, it may be flow-divided to 1/10 to 1/50 with a gas flow divider.

(8) When a high frequency induction heater is used, tin and chromium oxide powder shall be used as ignition improvers. The additional amount thereof shall be in accordance with 3.2 Note (15), as appropriate.

(9) The sample herein shall be treated as described in 3.2 Note (8).

(10) Preliminarily analyze the standard sample of a known carbon content in the same operation, regulate the quantity of electricity of one count so that the read of the counter of indication circuit coincides with the carbon content, or otherwise obtain the relation curve between the read of the counter of indication circuit and the carbon content, allow it to be the working curve, insert the read of the counter when the sample is analyzed and obtain the carbon content.

- (¹¹) The complete oxidation of sample shall be confirmed and the test of the apparatus by standard sample shall be respectively in accordance with 3.2 Note (¹³), as appropriate.

4. Method for Determination of Silicon

4.1 Classification of Methods The method for determination of silicon shall be in accordance with either of the following methods:

- (1) Silicon Dioxide Gravimetric Method This method applies to the sample of not less than 0.1 % in silicon content.
- (2) Molybdenum Blue Absorptiometry This method applies to the sample of under 1 % in silicon content.

4.2 Silicon Dioxide Gravimetric Method

4.2.1 Summary A sample is decomposed with the mixed acid of hydrochloric acid and nitric acid, added with perchloric acid, evaporated by heating and silicon is made to be insoluble silicon dioxide. After filtration, it is ignited to constant weight. Then, it is added with hydrofluoric acid and silicon dioxide is volatilized by evaporation. Its loss is measured.

4.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid (1+10)
- (2) Perchloric acid (60 %)
- (3) Hydrofluoric acid (46 %)
- (4) Sulfuric acid (1+3)
- (5) Mixed acid (hydrochloric acid 1, nitric acid 1 and water 1)
- (6) Ammonium tartrate solution 15 g tartaric acid is dissolved with 500 ml water, added with 15 ml aqueous ammonia and diluted to 1000 ml with water.

4.2.3 Weighing Out Amount of Sample For the sample, 3.0 g shall be weighed out.

4.2.4 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Weigh out a sample, transfer it into a beaker (300 ml), cover it with a watch glass, add 50 ml mixed acid, decompose it by quietly heating, add 40 ml perchloric acid and continue to heat it for 15 to 20 min to a extent that chromium is oxidized to red dichromic acid and the vapour of perchloric acid is refluxed along the wall of beaker.

- (2) After standing to cool for a while, add about 120 ml warm water, dissolve salts by agitation, immediately filter it with a filter paper (Class 5 B), rub off silicon dioxide adhered to the wall of a beaker by using the glass bar with a rubber tube and transfer it onto the filter paper. Wash it alternately each five times with warm water and warm hydrochloric acid (1+10) at first and with warm water at last until the reaction of iron ion disappears in the filtrate⁽¹⁾.
- (3) Transfer the residue together with the filter paper into a platinum crucible. After drying, incinerate the filter paper at a low temperature. Thereafter, ignite it at not lower than 1100°C to constant weight, let it stand to cool in a desiccator and measure the mass.
- (4) Then, wet the residue with sulfuric acid (1+3), add 3 to 5 ml hydrofluoric acid⁽²⁾ and vaporize silicon dioxide and sulfuric acid by carefully heating. Thereafter, ignite it at not lower than 1100°C to constant weight, let it stand to cool in a desiccator and measure the mass.

4.2.5 Calculation The content of silicon in sample shall be calculated from the following formula:

$$\text{Silicon (\%)} = \frac{(w_1 - w_2) \times 0.4674}{W} \times 100$$

where

w_1 : mass of platinum crucible containing impure silicon dioxide ignited to constant weight at the first time (g)

w_2 : Mass of platinum crucible containing impurities ignited to constant weight at second time (g)

W : weighing out amount of sample (g)

Notes ⁽¹⁾ For washing silicon dioxide, warm ammonium tartrate solution may be used instead of warm water and warm hydrochloric acid to wash it about 3 to 4 times until the colour of iron salt adhered to the filter paper disappears.

⁽²⁾ The ignition residues of the hydrofluoric acid and sulfuric acid of the same amount as the used amount shall be obtained and added as the blank test value. However, the amount of ignition residue of hydrofluoric acid shall not exceed 0.04 mg per 1 ml thereof.

4.3 Molybdenum Blue Absorptiometry

4.3.1 Summary A sample is decomposed with hydrochloric acid and hydrogen peroxide water, added with ammonium molybdate and silicon is made to be silicomolybdic acid by heating. It is added with hydrofluoric acid and the influence of phosphorus, arsenic, iron, etc. are removed. Thereafter, silicomolybdic acid is reduced by adding ammonium ferrous sulfate and the absorbance of generated Molybdenum blue is measured.

4.3.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric Acid
- (2) Hydrofluoric Acid (4 %) 87 ml hydrofluoric acid (46 %) is diluted to 1000 ml with water and put in a polyethylene vessel to be stored.
- (3) Hydrogen Peroxide Water (30 %)
- (4) Ammonium Molybdate Solution 106 g ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ is dissolved by using warm water. After cooling, it is diluted to 1000 ml with water. For this solution, the precipitate is filtered at each use and the filtrate is used.
- (5) Ammonium Ferrous Sulfate Solution 300 g ammonium ferrous sulfate is dissolved with 500 ml water, added with 200 ml sulfuric acid (1+1) and diluted to 1000 ml with water.
- (6) Standard Silicon Solution (20 μg Si/ml) 0.428 g pure silicon dioxide which is preliminarily ignited at 1000°C and let to stand to cool in a desiccator, is weighed out into a platinum crucible, incorporated with 2.5 g sodium carbonate anhydride and fused. After cooling, the melt is extracted and dissolved by dipping it into the platinum dish or polyethylene beaker put with 100 ml warm water. Thereafter, the platinum crucible is washed with water and taken out. After cooling, it is filtered by using the filter paper (Class 5 B) put with a small amount of filter paper pulp and washed with sodium carbonate solution (1 w/v %). The filtrate and washings are transferred into a measuring flask of 1000 ml, diluted with water up to the marked line to prepare the stock solution of 0.2 mg Si/ml and put into a polyethylene vessel to be stored. For this solution, the silicon content is determined by gravimetric method at each service and diluted with water to prepare the standard silicon solution.

4.3.3 Weighing Out Amount of Sample For the sample, 0.10 g shall be weighed out.

4.3.4 Operation The determination operation shall be carried out in accordance with the following procedures:

- (1) Weigh out a sample, transfer it into an Erlenmeyer flask (200 ml), carefully add 15 ml hydrochloric acid⁽¹⁾ and 10 ml hydrogen peroxide water (30 %)⁽²⁾, put it on the low temperature portion of hot plate for about 30 sec⁽³⁾ and decompose most of the sample. Thereafter, add about 40 ml water, completely decompose it⁽⁴⁾ by heating on the hot plate for about 3 min and dip it into running water. After cooling, transfer it into a measuring flask of 250 ml by washing and dilute it up to the marked line by using water⁽⁵⁾.
- (2) Accurately and separately take 50 ml from this solution into two measuring flasks of 100 ml⁽⁶⁾, add 10 ml ammonium molybdate

solution to the first measuring flask, spray a small amount of water, wash out the ammonium molybdate solution adhered to the inside wall of flask, dip it into boiling water bath for 30 sec⁽⁷⁾, immediately dip it into running water and regulate the temperature of solution at about 30°C. Further, without adding ammonium molybdate solution to the second measuring flask, regulate the temperature of solution at about 30°C.

- (3) Add 20 ml hydrofluoric acid to them, mix them by slightly shaking, add 5 ml ammonium ferrous sulfate solution within 30 sec⁽⁸⁾, mix them by shaking, dilute it up to the marked line by using water and further sufficiently mix them by shaking.
- (4) After about 1 min⁽⁹⁾, take a portion of those solutions into the absorption cell of a photometer and measure each absorbance at near 810 nm in wavelength ⁽¹⁰⁾⁽¹¹⁾⁽¹²⁾⁽¹³⁾.

4.3.5 Calculation The amount of silicon corresponding to each of them shall be obtained from the working curve prepared in 4.3.6 and the content of silicon in sample shall be calculated from the following formula ⁽¹⁴⁾:

$$\text{Silicon (\%)} = \frac{A-B}{W \times C} \times 100$$

where

A: silicon equivalent amount detected from the solution in the first measuring flask (g)

B: silicon equivalent amount detected from the solution in the second measuring flask (g)

W: weighing out amount of sample (g)

C: aliquot ratio of sample solution

4.3.6 Preparation of Working Curve The standard sample having a known silicon content is used, operated in accordance with the procedures of 4.3.4 (1) to (4) and the relation curve between the obtained absorbance and the amount of silicon is prepared to be the working curve. Further, by using the mixed sample obtained by stepwise adding 0 to 50.0 ml standard silicon solution to 0.100 g pure iron instead of standard sample, the working curve may be prepared. However, in the case, the correction shall be necessarily carried out by utilizing the amount of silicon in pure iron as the blank test value.

Notes ⁽¹⁾ The using amount of hydrochloric acid shall necessarily be 15 ml so as to obtain the concentration of acid suitable for adding ammonium molybdate solution, that is, a range of 0.6 to 0.9 N capable of obtaining a fixed absorbance.

⁽²⁾ Hydrogen peroxide water of a high concentration (30 %) shall be used to utilize the intensive decomposition force.