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JAPANESE INDUSTRIAL STANDARD

Methods for Chemical Analysis of Metallic Silicon

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Methods for Chemical Analysis of
Metallic SiliconG 1322-1977
(Reaffirmed: 1980)1. Scope

This Japanese Industrial Standard specifies the methods for determination of silicon, carbon, phosphorus, sulfur, iron, aluminium and calcium in metallic silicon.

2. General Matters

General matters common to the methods for chemical analysis shall be in accordance with JIS G 1301 and JIS K 0121.

3. Method for Determination of Silicon

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

- (1) Gravimetric method
- (2) Neutralization titrimetric method

3.2 Gravimetric Method

3.2.1 Summary A sample is fused with fusing mixture, added with hydrochloric acid and perchloric acid, evaporated by heating and silicon is made insoluble silicon. The residue is ignited and its mass is measured. Thereafter, silicon dioxide is vapourized by treatment with hydrofluoric acid and the loss thereof is measured.

Applicable Standards:

JIS G 1301-General Rules for Chemical Analysis of Ferro-alloys

JIS K 0121-General Rules for Atomic Absorption Spectrochemical Analysis

JIS K 8005-Standard Substances for Volumetric Analysis

JIS K 8006-Fundamental Articles on Volumetric Determinations

3.2.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1 + 1, 1 + 2, 1 + 10)
- (3) Perchloric acid
- (4) Hydrofluoric acid
- (5) Sulfuric acid (1 + 1, 1 + 3)
- (6) Sodium hydroxide
- (7) Fusing mixture [sodium peroxide 2 + sodium carbonate (anhydrous) 1]

3.2.3 Weighing Out Amount of Sample 0.20 g of the sample shall be weighed out to the nearest 0.1 mg.

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

- (1) Weigh out a sample, transfer it into a nickel crucible (30 ml), add 5 g fusing mixture, sufficiently mix them by stirring, cover it with 1 g fusing mixture, cover it with a cover and gradually heat it until the contents are melted down. Thereafter, fuse them at approx. 700°C (dark red heat) for about 5 min while mixing them by shaking at times.
- (2) After standing to cool, put the crucible into the beaker (500 ml) containing 60 ml hydrochloric acid (1 + 2), elute the melt, wash the crucible with water and take it out. Further, add 40 ml perchloric acid ⁽¹⁾, evaporate it by heating on a sand bath and successively continue to heat it for about 15 min under the state in which the vapour of perchloric acid is refluxed along the inside wall of beaker.
- (3) After standing to cool, dissolve soluble salts by adding 20 ml hydrochloric acid (1 + 1) and approx. 100 ml warm water and immediately filter it by using a filter paper (Class 5 A). Rub off the residue stuck to the inside wall with a policeman, transfer it onto the filter paper by washing and wash it at first 5 times with warm hydrochloric acid (1 + 10) and then with warm water until the reaction of iron ion disappears in the filtrate.
- (4) Receive the filtrate with a beaker (500 ml), add 10 ml perchloric acid ⁽²⁾, evaporate it by heating on a sand bath and continue to heat it for about 15 min under the state in which the vapour of perchloric acid is refluxed along the inside wall of beaker.
- (5) Use a filter paper (Class 5 B) in accordance with the operation of (3), filter it and wash it.
- (6) Transfer the residue on the filter papers obtained by the operation of two times together with the filter papers into a platinum crucible and dry them. Then, gradually heat to carbonize the filter papers. Thereafter, carefully incinerate them, ignite them at approx. 1100°C to constant weight and measure the mass.

- (7) Wet the residue in the platinum crucible with sulfuric acid (1 + 3), add 3 to 5 ml hydrofluoric acid, carefully heat it, vapourize silicon dioxide and sulfuric acid, ignite it again at approx. 1100°C to constant weight and measure its mass.

3.2.5 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 (g)

w_2 : mass of platinum crucible containing impurities (g)

W : weighed out amount of sample (g)

Notes (1) 40 ml sulfuric acid (1 + 1) may be used instead of perchloric acid.

(2) When sulfuric acid has been used, it is not required to add perchloric acid.

Remarks 1. 5 g sodium hydroxide may be used instead of fusing mixture. In that case, the operation shall be carried out as follows:

Sufficiently mix the sample and sodium hydroxide. After sufficiently dehydrating them on a hot plate, carefully fuse them by gradually raising temperature. After standing to cool, put the crucible into the polyethylene beaker (300 ml) containing approx. 100 ml warm water, elute the melt, wash the crucible with water and take it out. Transfer this solution into the beaker (500 ml) containing 20 ml hydrochloric acid by washing, add 40 ml perchloric acid, heat it on a sand bath and successively continue to heat it for about 15 min under the state in which the vapour of perchloric acid is refluxed along the inside wall of beaker. Hereafter, operate it in accordance with the procedures of 3.2.4 (3) to (7).

2. Silicic acid may be dehydrated by using hydrochloric acid. In that case, the operation shall be carried out as follows:

Fuse the sample in accordance with the procedure of 3.2.4 (1), put it into the beaker (500 ml) containing 60 ml hydrochloric acid (1 + 2) and elute the melt. Thereafter, wash the crucible with water and take it out. Evaporate the solution on a water bath to dryness and heat it for about 1 h in an air bath at approx. 120°C. Thereafter, operate it in accordance with the procedures of 3.2.4 (3) to (7). However, allow the amount of perchloric acid used in 3.2.4 (4) to be 40 ml.

3.3 Neutralization Titrimetric Method

3.3.1 Summary A sample is decomposed with nitric acid, potassium nitrate and hydrofluoric acid and potassium silicofluoride is precipitated. This precipitate is dissolved with warm water and titrated with sodium hydroxide standard solution.

3.3.2 Reagents The reagents shall be as follows:

- (1) Hydrochloric acid
- (2) Nitric acid (1 + 1)
- (3) Hydrofluoric acid
- (4) Sodium hydroxide
- (5) Potassium hydroxide
- (6) Fusing mixture [sodium peroxide 1 + potassium carbonate (anhydrous) 5]
- (7) Potassium nitrate
- (8) Potassium nitrate solution (5 w/v %) Because potassium nitrate solution (5 w/v %) is occasionally alkalized, it shall be preliminarily neutralized with nitric acid in that case.
- (9) N/2 sodium hydroxide standard solution (20.00 g NaOH/l)
The preparation and standardization method thereof shall be in accordance with 2. (13) of JIS K 8006.
- (10) Phenolphthalein solution 0.5 g phenolphthalein is dissolved with 100 ml ethyl alcohol (95 v/v %).

3.3.3 Weighing Out Amount of Sample 0.10 g of the sample shall be weighed out to the nearest 0.1 mg.

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

- (1) Weigh out a sample, transfer it into a polyethylene beaker (300 ml), add 30 ml nitric acid (1 + 1) and 3 g potassium nitrate and decompose them by adding little by little 10 ml hydrofluoric acid while mixing them by shaking.
- (2) Dilute the amount of solution to approx. 80 ml by adding 5 ml hydrochloric acid and water. After heating it for about 15 min on a water bath, add a small amount of filter paper pulp, let them stand still for about 30 min while cooling them to approx. 15°C or less and complete the precipitate of potassium silicofluoride.
- (3) Filter it by using a filter paper (Class 5 A) with a polyethylene funnel while cooling it to 15°C or less and sufficiently wash it with potassium nitrate solution cooled to 15°C or less until blue litmus test paper does not turn to red ⁽¹⁾.

Transfer the precipitate together with the filter paper into an Erlenmeyer flask (200 ml), add approx. 50 ml warm water and sufficiently mix them by shaking to crush the filter paper.

- (4) After boiling, immediately add several drops of phenolphthalein solution, add N/2 sodium hydroxide standard solution near the end point at a time, further add several drops phenolphthalein solution, titrate it again with N/2 sodium hydroxide standard solution and allow the point at which the solution turns to faint red to be the end point.

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

$$\text{Silicon (\%)} = \frac{V \times 0.003511}{W} \times 100$$

where V: used amount of N/2 sodium hydroxide standard solution (ml)

W: weighed out amount of sample (g)

Note (1) In general, it is sufficient to wash about 15 times.

Remark: When a sample is not decomposed with hydrofluoric acid and nitric acid, the operation shall be carried out as follows:

Weigh out the sample, transfer it into a nickel crucible (30 ml), add fusing mixture or sodium hydroxide or potassium hydroxide and mix them. Cover them and gradually heat them until the contents are melted down. Thereafter, fuse them at approx. 700°C (dark red heat) for about 5 min while mixing them by shaking at times. After standing to cool, add a small amount of warm water to the crucible, dissolve the melt by quietly heating and gradually transfer it into the polyethylene beaker (300 ml) containing 50 ml nitric acid (1 + 1) by washing. Add 3 ml hydrochloric acid to the crucible to dissolve the residue stuck to the inside wall and further sufficiently wash it with water.

Completely dissolve it by heating on a water bath. After diluting the solution to approx. 80 ml by adding water, add 10 ml hydrofluoric acid and 3 g potassium nitrate, mix them by stirring and heat it for about 15 min on a water bath. Add a small amount of filter paper pulp, let it stand still for about 30 min while cooling it at 15°C or less and complete the precipitate of potassium silicofluoride. Hereafter, carry out the operation in accordance with the procedures of 3.3.4 (3) and (4).

4. Methods for Determination of Carbon

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

- (1) Neutralization titrimetric method
- (2) Conductometric method
- (3) Coulometric method

4.2 Neutralization Titrimetric Method

4.2.1 Summary A sample is ignited in oxygen current and carbon is completely burnt to carbon dioxide. The carbon dioxide together with oxygen is conducted into the carbon dioxide absorption apparatus preliminarily containing a definite amount of sodium hydroxide standard solution and carbon dioxide is absorbed. Thereafter, the solution is titrated with sulfuric acid standard solution.

4.2.2 Reagents The reagents shall be as follows:

- (1) Sulfuric acid (1 + 1)
- (2) Chromic acid saturated sulfuric acid Sulfuric acid (specific gravity 1.82) is saturated with potassium bichromate or chromic anhydride and its supernatant is used.
- (3) Barium hydroxide solution (saturated, approx. 4 w/v %) The water from which carbon dioxide is removed by boiling, is used.
- (4) Oxygen That of not less than 99.5 v/v % in purity, is used.
- (5) Copper oxide Granular or linear copper oxide
- (6) Ignition improver High pure iron, copper, tin or the like having carbon content as low as possible
- (7) Asbestos or glass wool
- (8) Soda lime or sodium hydroxide For the sodium hydroxide, granular sodium hydroxide is used.
- (9) Active alumina Active alumina of rice grain size is used.
- (10) Manganese dioxide
- (11) Potassium permanganate solution (5 w/v %)
- (12) N/100 sodium hydroxide solution 0.4 g sodium hydroxide is dissolved with the water from which carbon dioxide is preliminarily removed by passing oxygen or the like to make 1 l. the solution is stored by attaching the absorption tube packed with soda lime or sodium hydroxide to the vessel so that oxidizing gases such as carbon dioxide or the like do not enter from the air and the solution is taken out by using an automatic burette. It is not required to determine the factor of this solution.

- (13) N/100 sulfuric acid standard solution 0.3 ml sulfuric acid is diluted to 1 l with the water from which carbon dioxide is removed. The factor of this solution is determined in accordance with 2. (6) of JIS K 8006 as appropriate.
- (14) Phenolphthalein solution 0.2 g phenolphthalein is dissolved with 100 ml ethyl alcohol.

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

- (1) Oxygen Purifying Train The oxygen purifying train, which aims at removing the carbon dioxide or organic gas and others which are contained in oxygen and at cleaning and drying oxygen, is constructed by successively connecting ⁽²⁾ the tube (a) packed with granular copper oxide heated at 800 to 850°C, an empty bottle and the gas cleaning bottle (b) ⁽¹⁾ containing chromic acid saturated sulfuric acid, and the tube or column (c) (c') packed with soda lime or sodium hydroxide and active alumina. However, when pure oxygen is used and the use of copper oxide tube (a) is not required, this cleaning train may be omitted.
- (2) Combustion Furnace The combustion furnace, for which the tubular electric furnace (d) of 200 to 300 mm in length is used, can keep a length of approx. 150 mm of its central part at a fixed temperature. Its temperature is regulated by controlling electric current and the temperature ⁽³⁾ just above the combustion tube is measured with a pyrometer.

The porcelain combustion tube (e) of approx. 24 mm in inside diameter having a length capable of protruding its both ends by approx. 200 mm is inserted into the furnace. Asbestos or glass wool is packed in the combustion tube over approx. 50 mm at the rear of inserted position of combustion board [refer to Attached Fig. 1 (Part 1)].

A high frequency induction heater may be used instead of the tubular electric furnace (refer to Attached Fig. 2). This apparatus is composed of the quartz vertical combustion tube of 30 to 44 mm in outside diameter, 26 to 37 mm in inside diameter and 200 to 220 mm in length, the heating coil of 35 to 55 mm in height and 4 to 5 turns in winding number wound outside and slightly downward from the center of combustion tube, and the high frequency oscillator supplying high frequency current thereto and if necessary, is attached with an oxygen flowmeter (0 to 2000 ml/min) and a time switch.

Further besides this, the metallic caps are airtightly attached by using heat resisting rubber at the both ends, from which the combustion tube is easily replaced. The upper cap is connected to a carbon dioxide absorption apparatus and the lower cap is connected to an oxygen purifying train. When the crucible is put on a receiving table and the lower cap is airtightly kept, the crucible is located to become approximately at the center of heating coil.

- (3) Carbon Dioxide Absorption Apparatus In order to remove the sulfur dioxide generated by combustion of the sample, the gas cleaning bottle containing approx. 5 ml of the solution acidified by adding 1 ml sulfuric acid (1 + 1) to 10 ml potassium manganate solution (5 w/v %), or the tube packed with manganese dioxide is connected to the rear of combustion tube. The carbon dioxide absorption apparatus is principally composed of the spiral absorption tube (h) of 4 mm in inside diameter, 1400 to 1600 mm in length, 45 to 80 mm in winding diameter, 10 to 6 in winding number and approx. 80 mm in height, containing a fixed amount of N 100 sodium hydroxide solution. While mixed gas becomes small bubbles and passes there-through, carbon dioxide is absorbed and the solution circulates. To observe the carbon dioxide which passes without being absorbed with the absorption tube, the inspection trap (i) containing approx. 5 ml barium hydroxide solution is connected to the rear of this absorption tube (h).

Further, a three-way cock (n), a collection bottle (l) and leveling bottle (m) may be attached between the three-way cock (k) and the cock (j). The operation in that case shall be in accordance with Remark.

- (4) Porcelain Boat and Porcelain Boat Cover or Crucible and Crucible Cover They are preliminarily blank-burnt at a temperature as high as possible and the blank test value is to be lowered. When a number of boats are blank-burnt at a time, after cooling, they are taken out with a pincette and stored in a desiccator without being coated with grease and the like. That having a high blank test value due to the storage for a long time shall not be used and is blank-burnt again.

4.2.4 Weighing Out Amount of Sample and Additional Amount of Ignition Improver 1.0 g of a sample (4) shall be weighed out to the nearest 10 mg, joined by (5) ignition improver and sufficiently mixed.

4.2.5 Operation

4.2.5.1 In the Case of Using Tubular Electric Furnace The determination operation shall be carried out in accordance with the following procedures:

- (1) Successively connect the apparatus of 4.2.3 (2), heat the combustion tube, raise the temperature in the tube to 1400 to 1450°C (3) and confirm (6) the airtightness of apparatus. Thereafter, cover the porcelain boat containing the sample and ignition improver weighed out with the porcelain boat cover, put it into the end part of combustion tube and airtightly attach the sample insertion tube (f) thereto. Open the three-way cock (k) toward the open air and pass oxygen at a rate of 200 to 300 ml per minute for about 5 min. After completely exhausting the air in combustion tube, open the three-way cock (k) toward the carbon dioxide absorption apparatus (h) side, accurately take 20 to 30 ml N/100 sodium hydroxide solution into the carbon dioxide absorption apparatus (h) passing little by little oxygen by regulating the cock (j), add 2 to 3 drops phenolphthalein solution as indicator, attach the inspection trap (i) and close the cock (j). When the sample insertion tube is not used, exhaust the air in combustion tube in accordance with the above-mentioned operation as appropriate and prepare the absorption apparatus.

- (2) Then, operate the insertion bar by using a magnet from the outside, push the porcelain boat into the maximum temperature part of the tube and return the insertion bar to the original position immediately ⁽⁷⁾.

Preheat about 3 min while so adjusting oxygen flow rate that the pressure in the tube may not be reduced even the sample begins to burn.

- (3) Gradually open the cock (j) to regulate the flow rate of oxygen passing through the inspection trap (i) to be 40 to 60 ml per minute, burn the sample by passing it for 10 min, conduct the mixed gas of oxygen and carbon dioxide into the carbon dioxide absorption apparatus (h) to make absorb carbon dioxide completely ⁽⁸⁾.
- (4) After removing the inspection trap (i), increase the flow rate of oxygen so that the absorption solution is quickly circulated, insert the tip of burette into the mouth of carbon dioxide absorption tube (h), pour N/100 sulfuric acid standard solution while moving it by shaking and when the colour of the solution reserved in the bulb part of carbon dioxide absorption apparatus (h) turns to faint pink, stop the pouring. Continue to titrate it by adding the following one drop when the solution in the spiral tube returns to the bulb part and turns to uniform pink, and allow the point at which faint pink remains in the solution to be the end point ⁽⁹⁾.
- (5) Use the porcelain boat containing ignition improver to carry out a blank test in accordance with the procedures of above-mentioned (1) to (4) as appropriate.

4.2.5.2 In the Case of Using High Frequency Induction Heater The determination operation shall be carried out in accordance with the following procedures:

- (1) Connect the apparatus of 4.2.3 ⁽²⁾, and confirm its airtightness ⁽⁶⁾. Thereafter, close the three-way cock (j) and let the three-way cock (k) open toward the open air.
- (2) Cover the crucible containing the sample and ignition improver weighed out with the crucible cover, insert it into the combustion tube, airtightly stopper it, open the oxygen switching valve (F) and the flow rate regulation valve (E), feed oxygen at a rate of approx. 300 ml per minute with observing the flow-meter (G) and expel the air in combustion tube. Thereafter, close the three-way cock (k). Accurately take 20 to 30 ml N/100 sodium hydroxide solution into the carbon dioxide absorption apparatus (h), add 2 to 3 drops of phenolphthalein solution thereto and connect the inspection trap (i) and the flow meter (o).
- (3) Regulate the flow rate regulation valve (E) under the state in which the cock (k) or (j) is closed and turn on the high frequency switch (C). The combustion starts immediately and the pressure becomes negative, then suitably open the flow rate regulation valve (E). When the cock (k) or (j) is opened

after the pressure becomes positive, the combustion gas flows into the carbon dioxide absorption apparatus (h) and carbon dioxide is absorbed and excess oxygen or the like is discharged into the air via the flow meter (o). Allow the flow rate in that case to be 40 to 60 ml per minute and regulate it with the flow rate regulation valve (E) and the cock (k) or (j) ⁽¹⁰⁾. The combustion is completed in 5 min, then stop oscillation by pushing the disconnecting switch (I), further feed oxygen for 5 min and allow carbon dioxide to be completely absorbed ⁽⁹⁾. Hereafter, carry out the operation in accordance with the procedures of 4.2.5.1 (4) and (5).

4.2.6 Calculation The content of carbon in sample shall be calculated from the following formula:

$$\text{Carbon (\%)} = \frac{(V_1 - V_2) \times 0.000120}{W} \times 100$$

where V_1 : used amount of N/100 sulfuric acid standard solution in blank test (ml)

V_2 : used amount of N/100 sulfuric acid standard solution in main test (ml)

W : weighed out amount of sample (g)

- Notes
- (1) When chromic acid saturated sulfuric acid turns to green, its oxidizing force disappears. Therefore, it shall be renewed before that.
 - (2) Because it is feared that the rubber tube absorbs carbon dioxide, glass tubes shall be used for respective contacts of apparatus and both ends thereof are closely contacted and supported with rubber tube or the like.
 - (3) The difference between the indication temperature of pyrometer and the temperature in combustion tube shall be carefully and necessarily corrected.
 - (4) A sample shall be kept from adhering especially with oils. If necessary, it is sufficiently cleaned with alcohol, ether, etc. and stored in a clean glass bottle. Further, a metallic spoon is used for its handling.
 - (5) The additional amount of ignition improver shall be 2 to 5 times the amount of sample.
 - (6) Before determination, the following airtightness test shall be necessarily carried out to take cares for airtightness.

Close the three-way cock (k) and feed oxygen. After standing for a while, confirm that the bubble of oxygen is not generated in the gas cleaning bottle (b) containing chromic acid saturated sulfuric acid and stop the feed of oxygen. If the bubble of oxygen is generated, the presence of inferior airtightness between the gas cleaning bottle (b) and the three-way cock (k) is indicated.

- (7) When the sample insertion tube is not used, the porcelain boat is directly pushed into the maximum temperature part of the tube and immediately stopper it tightly.
- (8) Though the barium hydroxide saturated solution in the inspection trap does not generally become white cloudy in this operation, if it becomes cloudy, the test shall be carefully operated again.
- (9) Though the state in which pink remains slightly continues for a while when N/100 sulfuric acid standard solution is added, the judgement of end point is not so difficult when accustomed.
- (10) When a large amount of oxygen is used for combustion and the regulation is difficult, it is preferable to grasp the pressure in the combustion tube by installation of a manometer.

Remark: When a collection bottle is used, the operation shall be carried out as follows:

Successively connect the apparatus in 4.2.3, heat the combustion tube, raise the temperature in the tube to 1400 to 1450°C ⁽³⁾ and confirm the airtightness ⁽⁶⁾. Thereafter, put the porcelain boat containing the weighed out sample ⁽⁴⁾ and ignition improver ⁽⁵⁾ into the end part of combustion tube and airtightly attach the sample insertion tube (f). Open the three-way cock (k) to the open air and pass oxygen at a rate of 200 to 300 ml per minute for about 5 min. After completely exhausting the air in the combustion tube, open the three-way cock (k) toward the collection bottle side and the three-way cock (n) toward the carbon dioxide absorption apparatus (h) side, accurately take 20 to 30 ml N/100 sodium hydroxide solution into the carbon dioxide absorption apparatus (h) while passing oxygen little by little, add 2 to 3 drops phenolphthalein solution as indicator, attach the inspection trap (i), close the cock (j) and allow the three-way cock (n) to be open toward the collection bottle side.

Then, operate the insertion bar by using a magnet from the outside, push the porcelain boat into the maximum temperature part in the tube and immediately return the insertion bar to the original position. After preheating for about 3 min, burn the sample by passing oxygen and complete the combustion when the gas fills about one half the capacity of bulb part of collection bottle (l). Thereafter, lower the leveling bottle (m), collect the mixed gas of carbon dioxide and oxygen near to the lowest part of collection bottle (l), close the three-way cock (k) and stop the feed of oxygen. Then, place the leveling bottle (m) at the upper position of collection bottle (l), open the three-way cock (n) to the carbon dioxide absorption apparatus (h) side, regulate the cock (j), conduct the collection gas into the carbon dioxide

apparatus (h) at a rate of 40 to 60 ml per minute and allow carbon dioxide to be completely absorbed. Thereafter, open the cock (k) and pass oxygen.

Hereafter, carry out the operation in accordance with the procedures of 4.2.5.1 (4) and (5).

4.3 Conductometric Method

4.3.1 Summary A sample is ignited in oxygen current and carbon is completely burnt to carbon dioxide. It is absorbed with alkaline solution and the change of the electric conductivity of alkaline solution before and after absorption of carbon dioxide is measured.

4.3.2 Reagents The reagents shall be as follows:

- (1) Sulfuric acid (1 + 1)
- (2) Alkaline solution Prepare the sodium hydroxide, potassium hydroxide or barium hydroxide solution of suitable concentration level as N/10 to N/200 according to the using apparatus. That is, prepare 1 N alkaline solution by using the pure water from which carbon dioxide is removed, to be the stock solution, then dilute the stock solution by using the pure water from which carbon dioxide is removed by passing the air from which carbon dioxide is removed or oxygen for a long time, prepare alkaline solution of a specific concentration, transfer it into the polyethylene vessel attached with the carbon dioxide absorption tube packed with soda lime or sodium hydroxide to be stored and take it out by using an automatic burette or the like.
- (3) Oxygen The oxygen of not less than 99.5 v/v % in purity
- (4) Ignition improvers Tin, copper, iron, etc. of high purity having carbon content as low as possible
- (5) Asbestos or quartz wool
- (6) Manganese dioxide
- (7) Potassium permanganate solution (5 w/v %)

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

- (1) Oxygen Purifying Train It is in accordance with the oxygen purifying train of 4.2.3 (1), as appropriate.

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

- (2) Combustion Furnace It is in accordance with the combustion furnace of 4.2.3 (2), as appropriate. However, asbestos is packed in the combustion tube, or the iron oxide powder collection tube packed with asbestos or quartz wool is connected to the rear of combustion tube.

Further, to remove the sulfur dioxide generated by combustion of the sample, the gas cleaning bottle containing approx. 5 ml solution acidified by adding 1 ml sulfuric acid (1+1) to 10 ml potassium permanganate solution (5 w/v %), or the tube packed with manganese dioxide is connected to the rear of combustion tube.

Further, the inlet of combustion tube may be opened if excess oxygen is exhausted into the air therefrom and the infiltration of air into the tube is prevented. Instead of the tubular electric furnace, the high frequency induction heater (refer to Attached Fig. 2) may be used.

- (3) Electric Conductivity Measuring Apparatus The electric conductivity measuring apparatus is principally composed of the unit in which the electrodes for measuring electric conductivity are enclosed in the spiral absorption tube containing a fixed amount of alkaline solution in order to absorb the carbon dioxide exhausted from the combustion tube, and in the spiral absorption tube containing a fixed amount of alkaline solution for comparison reference use respectively and are put into the thermostatic bath capable of keeping at a fixed temperature. The determination pump or vacuum pump for feeding combustion gas into the absorption tube at a fixed flow rate, a gas reservoir and a flowmeter are attached to the front or the rear of the carbon dioxide absorption spiral tube.
- (4) Recorder It takes out the record as the change amount of electric conductivity obtained with Wheatstone Bridge to be indicated with the value corresponding to the content of analytical constituent by means of an automatic null-balance recorder or the like.

Further, for this purpose either recording by a recording paper of direct reading on a scale may be applied.

- (5) Porcelain Boat and Porcelain Boat Cover or Crucible and Crucible Cover They shall be preliminarily blank-burnt at temperature as high as possible.

4.3.4 Weighing Out Amount of Sample and Additional Amount of Ignition Improver The optimum amount of sample ⁽¹⁾ for the using apparatus shall be weighed out and its amount shall be confirmed by analysis of the standard sample having a known carbon content. The sample is joined ⁽²⁾ by ignition improver and sufficiently mixed.

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

- (1) Raise the temperature in combustion tube to 1400 to 1450°C ⁽³⁾ ⁽⁴⁾ and keep the thermostatic bath of electric conductivity measuring apparatus at a fixed temperature. Then, turn on the switch of pump and pass oxygen through the apparatus. Put a fixed amount of alkaline solution into the electric conductivity measuring absorption tube, pass oxygen and regulate the zero point of electric conductivity measuring recorder.

- (2) Then, cover the porcelain boat in which the sample ⁽¹⁾ and ignition improver are weighed out with the porcelain boat cover, insert it into the central part of combustion tube and successively feed oxygen. When the sample is burnt and carbon dioxide starts to be absorbed in the alkaline solution, the pointer of recorder starts to move. After the indication value of the pointer is stabilized ⁽⁵⁾, stop the feed of oxygen, take out the porcelain boat and confirm that the oxidation of sample is completed.

4.3.6 Calculation The content of carbon in sample shall be calculated from the following formula:

$$\text{Carbon (\%)} = \frac{D \times F}{W} \times 100$$

where D : indication value of recorder

F : amount of carbon equivalent to unit scale of indication value of recorder (g)

W : weighed out amount of sample (g)

- Notes
- (¹) The handling of analysis sample is in accordance with 4.2 Note (⁴), as appropriate.
 - (²) The use of ignition improver is in accordance with 4.2 Note (⁵), as appropriate.
 - (³) The measurement of temperature is in accordance with 4.2 Note (³), as appropriate.
 - (⁴) The handling in the case of using a high frequency induction heater instead of a tubular furnace, is in accordance with 4.2.5.2, as appropriate.
 - (⁵) The standard sample having a known carbon content is preliminarily analysed by the same operation and existence of no difference between the indication value and the standard value is confirmed. If there is some difference, the difference shall be eliminated by regulation of the sensitivity of recorder.

4.4 Coulometric Method

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

4.4.2 Reagents The reagents shall be as follows:

- (1) Barium perchlorate absorption solution That of a suitable concentration according to the using apparatus, is prepared. 25 g barium perchlorate is generally dissolved with approx. 100 ml water, joined by 10 to 15 ml isopropyl alcohol and diluted to 500 ml with 500 ml water to be used.

- (2) Barium perchlorate electrolyte That of a suitable concentration is prepared according to the using apparatus. 15 to 20 g barium perchlorate is, as a rule, dissolved with water and diluted to 100 ml with water to be used.
- (3) Contrast electrode cell solution That of a suitable concentration is used according to the using apparatus. 25 g barium perchlorate and 10 to 20 g sodium chloride are, as a rule, dissolved with approx. 200 ml water, joined by 10 to 15 ml isopropyl alcohol and diluted to 500 ml with water to be used.
- (4) Barium carbonate
- (5) Oxygen That of 99.5 v/v % or more in purity
- (6) Ignition improver High pure tin, copper, iron, etc. having carbon content as low as possible
- (7) Oxidizing catalyst (platinum asbestos, copper oxide, etc.)
- (8) Soda lime or sodium hydroxide Granular sodium hydroxide is used.
- (9) Asbestos
- (10) Quartz wool or glass wool
- (11) Manganese dioxide

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

- (1) Oxygen Purifying Train The oxygen purifying train, which aims at removing the carbon dioxide or organic gas and others contained in oxygen to be used and at cleaning and drying oxygen, is constructed by connecting the small size electric furnace to heat the tube packed with oxydizing catalyst at approx. 800°C and the tube or column packed with soda lime or sodium hydroxide, or otherwise is in accordance with the oxygen purifying train of 4.2.3 (1), as appropriate.
- (2) Oxygen Pressure Regulator For the purpose of avoiding the incomplete combustion of sample due to shortage of oxygen, the oxygen pressure regulator capable of always keeping the pressure of oxygen in combustion tube constant, is used.
- (3) Combustion Furnace It is in accordance with the combustion furnace of 4.2.3 (2), as appropriate. Provided that, asbestos is packed in the combustion tube, or otherwise the iron oxide powder collection tube packed with quartz wool or glass wool is connected to the rear of combustion tube.

Further, if excess oxygen is exhausted to the open air from the sample inlet of combustion tube and the infiltration of air into the tube is prevented, the sample inlet of combustion tube may be opened. The high frequency induction heater (refer to Attached Fig. 2) can be used instead of the tubular electric furnace.