

JIS

JAPANESE INDUSTRIAL STANDARD

**Chromium ores — Determination
of sulfur content**

JIS M 8268—1990

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

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1. Scope

This Japanese Industrial Standard specifies the determination of sulfur content in chromium ores.

Remarks: Applicable Standards to this Standard are shown in the following:

- JIS K 8001 General Rules of Testing Methods for Reagents
- JIS K 8005 Standard Substances for Volumetric Analysis
- JIS M 8261 General Rules for Chemical Analysis of Chrome Ores
- JIS R 1306 Porcelain Combustion Boats for Chemical Analysis
- JIS R 1307 Porcelain Combustion Tubes for Chemical Analysis
- JIS R 1308 High Frequency Combustion Crucibles for Chemical Analysis
- JIS Z 2616 General Rules for Determination of Sulfur in Metallic Materials
- JIS Z 8401 Rules for Rounding off of Numerical Values

2. General Matters

General matters common to the determination shall be in accordance with JIS M 8261 and JIS Z 2616.

3. Division of Determination

The determination of sulfur content in chromium ores shall be in accordance with one of the following:

- (1) Combustion - Neutralization Titration Method This method applies to the sample not less than 0.005 wt % in sulfur content.
- (2) Combustion - Potassium Iodate Titration Method This method applies to the sample not less than 0.005 wt % in sulfur content.

- (3) Combustion - Infrared Absorption Method This method applies to the sample not less than 0.003 wt % in sulfur content. However, this is not applicable to the sample not less than 1 wt % in bound water content.

Reference: As to combustion-infrared absorption method, there are integral method and circulation method.

4. Combustion - Neutralization Titration Method

4.1 Summary Heat the sample at a high temperature in nitrogen or oxygen gas flow, let absorb the generated sulfur oxides in hydrogen peroxide water to make sulfuric acid, and titrate with sodium hydroxide standard solution.

4.2 Reagents Reagents shall be as follows:

- (1) Absorption Liquid Take hydrogen peroxide 3.5 ml, cool the water preliminarily expelled with carbon dioxide by boiling, and add it to dilute to approximately 1000 ml. Separately take a definite quantity of this solution, add 3 to 5 drops of mixed indicator of Methyl Red and Methylene Blue, titrate with 0.01 mol/l sodium hydroxide standard solution, according to the result add the required quantity of 0.01 mol/l sodium hydroxide standard solution to the mother liquor to neutralize, and put into a brown bottle to store. Use this solution with further neutralizing correctly at each use.
- (2) 0.01 mol/l Sodium Hydroxide Standard Solution (0.400 g NaOH/l) Prepare 0.1 mol/l sodium hydroxide standard solution, at each time of use cool water expelled of carbon dioxide by boiling preliminarily to add, and dilute correctly to 10 times and take it as the 0.01 mol/l sodium hydroxide standard solution. The preparation and storing method of 0.1 mol/l sodium hydroxide standard solution must be in accordance with 4.4 (20.4) [0.1 mol/l sodium hydroxide solution (4.000 g NaOH/l)] of JIS K 8001.

Further the standardizing method must be in accordance with preparation operation 4.6.1 (3) of body.

- (3) Mixed Indicator of Methyl Red and Methylene Blue Dissolve Methyl Red 0.125 g and Methylene Blue 0.083 g in a small quantity of ethanol (95) and dilute by ethanol (95) to 100 ml.

4.3 Apparatus The apparatus shall be composed of refining part of nitrogen or oxygen as carrier gas, sample heating part and sulfur dioxide absorption part and, as a rule, the following shall be used (Refer to Fig. 1).

- (1) Carrier Gas Refining Part As to carrier gas, in the case of using tubular electric resistance heating furnace for sample heating part, either nitrogen or oxygen is used and in the case of using high frequency induction heating furnace, oxygen is used.

The carrier gas refining part is the part to regulate the pressure and flow rate of carrier gas supplied from nitrogen or oxygen bomb and to remove the components to be hindrance for determination of sulfur such as sulfur oxides, organic sulfur compounds, water, etc. contained in carrier gas, which is composed of the carrier gas bomb, pressure reducing valve, flowmeter, oxidation tube, sulfur oxide absorption tube, dehydration tube, etc. and connected in this order to be used.

For this oxidation tube, a washing bottle (a) containing chromic-acid saturated sulfuric acid, for sulfur oxide absorption bottle, a tower (b) filled with soda lime or powdery sodium hydroxide, for dehydration tube, a washing bottle (c) containing sulfuric acid, and a tower (d) filled with silica gel, active alumina or magnesium perchlorate (anhydride) are used.

Further, in the case where impurities interfering the determination of sulfur are not contained in nitrogen or oxygen to be used, a part of this or all parts can be omitted.

- (2) Sample Heating Part The sample heating part is a part to hot-decompose the sample and composed of a combustion tube and heating furnace. It is used by connecting a carrier gas refining part at inlet of combustion tube and a sulfur dioxide absorption part at outlet. As to heating furnace there are the tubular electric resistance heating furnace and high frequency induction heating furnace, and either one of them is used.

- (a) Tubular Electric-resistance Heating Furnace As to the tubular electric-resistance heating furnace, as a rule, the following is used.

Make the heating furnace (f) to be approximately 30 mm in internal diameter, approximately 300 mm in length, and capable of keeping the length of approximately 150 mm on the middle part of furnace at the using temperature of Table 2 by heating with using on electric resistance heating element, and regulating the electriccurrent to adjust the temperature.

Insert into the furnace a porcelain combustion tube (e) (CT1 or CT2 of JIS R 1307) of approximately 600 to 700 mm in length, approximately 24 mm in bore, and capable of enduring the using temperature (Refer to Table 2), fit at its rear end a tapered ground-in glass cap (g) and clamp to the furnace wall with spring. Extrude the rear end of combustion tube from the furnace wall by 100 to 150 mm including the glass cap.

Further, place a shielding plate (h) between the glass cap and the furnace wall to make so as the heat from the heating furnace not to apply to the absorption bottle.

Measure the temperature just above the combustion tube (e) at the middle part of the furnace by using a thermocouple pyrometer. Because the indicating value of this pyrometer is generally different from the temperature in the combustion tube, obtain the difference, correct the indicating value and estimate the temperature in combustion tube.

For connection of combustion tube with carrier gas refining part, use a ground-in or heat resistant silicon plug.

Further, in the case of using a new combustion tube, while feeding-in the carrier gas at the using temperature blank burn and after the blank test value has been stabilized, use it.

Further, in case where the internal wall of combustion tube is stained with iron oxide or the like, wash it prior to use. However, when the stain in the combustion tube is remarkable and impossible to remove it sufficiently, exchange the combustion tube with a new one.

- (b) High-frequency Induction Heating Furnace As to the high-frequency induction heating furnace, as a rule, the following is used (Refer to Fig. 2).

The heating furnace is composed of a quartz combustion tube (external diameter 30 to 44 mm, bore 26 to 37 mm, and length 200 to 220 mm), heating coil wound around its outside (height 35 to 55 mm, number of winding 4 to 5 turns), high frequency oscillator, etc. When the sample is put into a porcelain crucible for high frequency combustion, this crucible is held approximately at the middle of heating coil and passed the electric current, it is to be so made that the temperature at which the sample is decomposed and the sulfur can be expelled completely can be obtained.

In the case of using this furnace, the carrier gas is limited to oxygen.

For supply of oxygen, a bypass circuit is provided and may be made in sequential operation with the moving of crucible-receiving stand.

Further, the outlet of combustion gas must prevent the condensation of sulfur dioxide with integrating with combustion tube or be capable of removing it in case of having condensed.

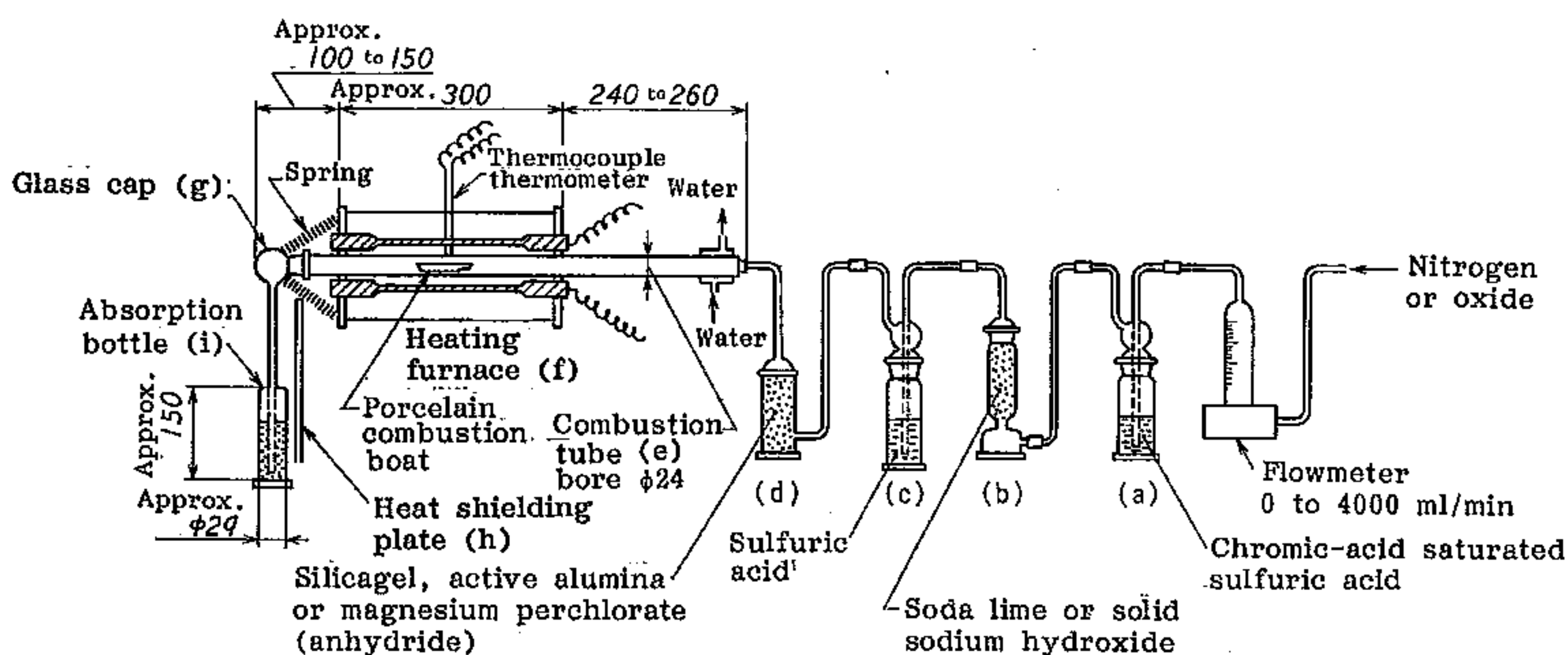
Further, the heating furnace must have such capability as to decompose the sample completely to oxidize sulfur in the sample and to feed out combustion gas from combustion tube.

- (3) Sulfur-dioxide Absorption Part Put absorption liquid specified in 4.2 (1) into absorption bottle (i), in the case of tubular electric-resistance heating furnace, through a glass cap (g), and in the case of high-frequency-induction heating furnace through a glass tube connected with heat resistant rubber tube or the like connect with the combustion tube.

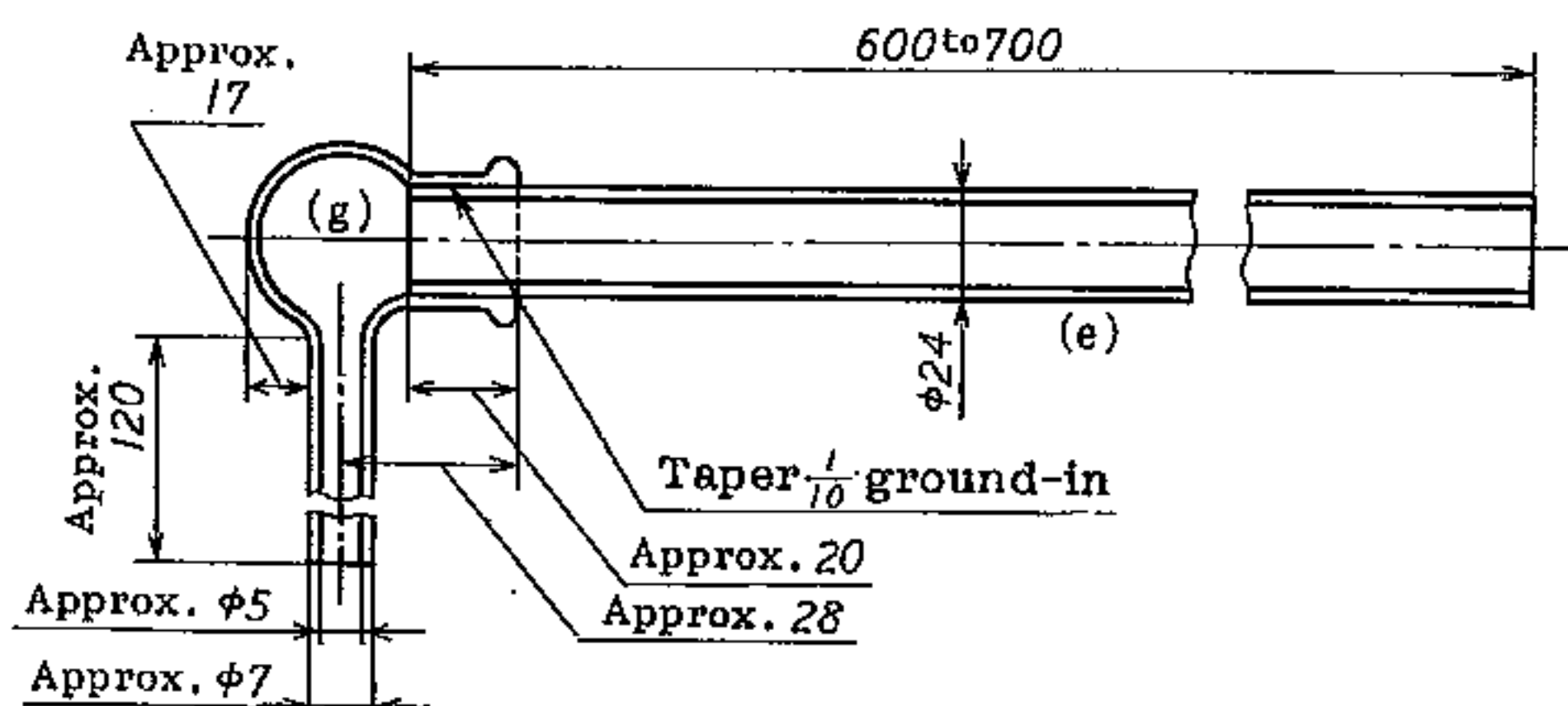
- (4) **Carrier Gas Bomb and Pressure Reducing Valve** The bomb to supply nitrogen or oxygen (in either cases not less than 99.5 %) to feed sulfur dioxide generated by decomposition of sample to absorption tube, in order to regulate the pressure and flow rate, is attached with a pressure reducing valve for respective gases. The pressure reducing valve should preferably be two step type.
- (5) **Flowmeter** The flowmeter has the purpose for monitor of flow rate of feeding carrier gas and generally, the rotameter for respective gases of 0 to 4000 ml per min degree is used. Because it does not require excessively high accuracy, other suitable meter may be used.

Fig. 1. Sulfur Determination Apparatus (Combustion - Neutralization Titration Method) (An example)

Unit: mm

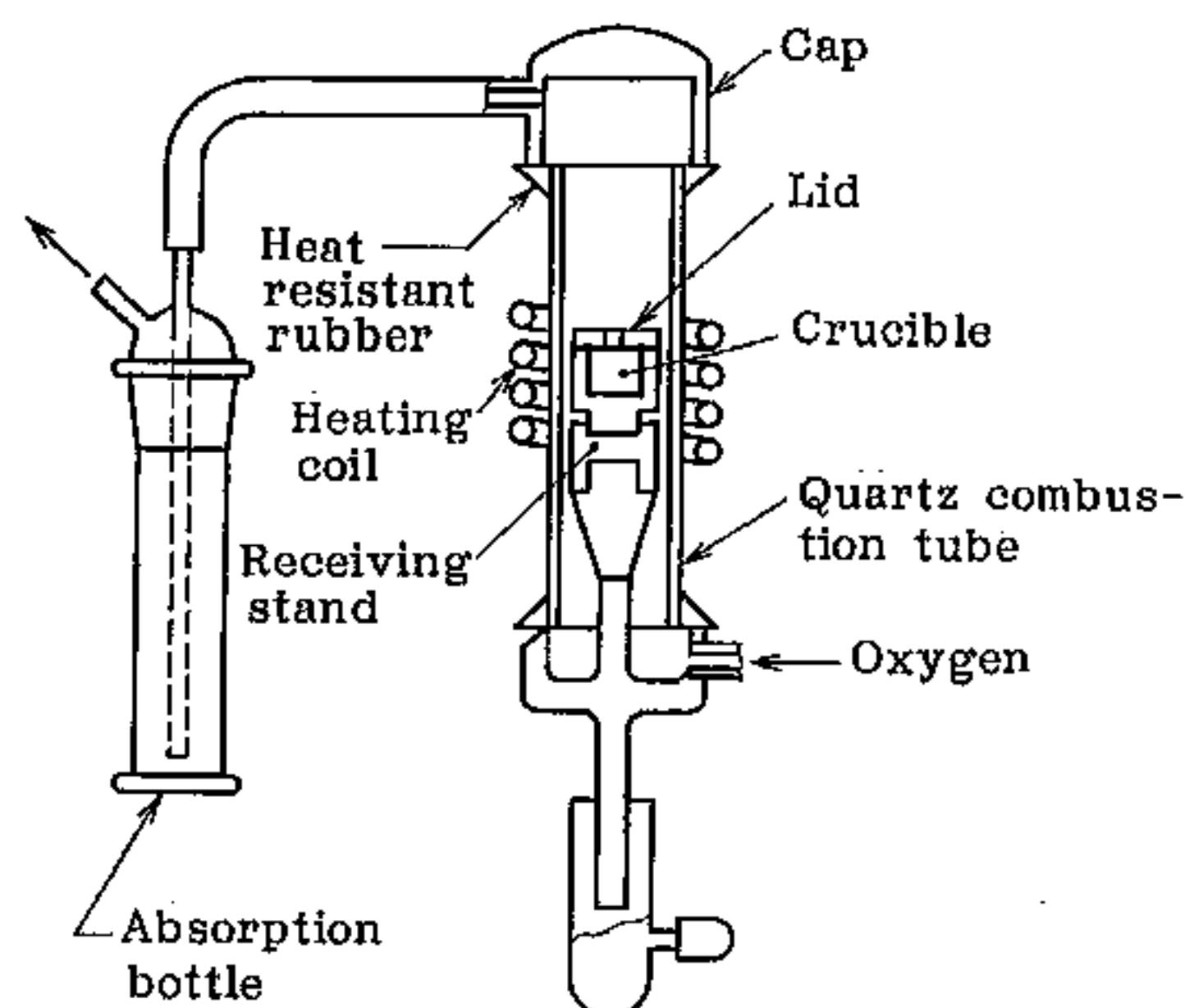


Combustion Tube Detail Drawing (An example)



Remarks: Dimensions indicate the approximate values.

Fig. 2. Sample Heating Part of High-frequency Induction Heating Furnace (An example)



4.4 Apparatus and Materials As to apparatus and materials the following shall be used, as a rule.

- (1) Porcelain Combustion Boat and Porcelain Combustion Boat Cover (hereafter referred to as the "boat" and the "cover") The boat to be used for tubular electric-resistance heating furnace is to be CB1 or CB2 of JIS R 1306. As to boat, as required, the cover is used. The cover is to be CBC1 of JIS R 1306.

The boat and cover to be used are blank burned at the same temperature as the heating temperature of sample while feeding preliminarily air or oxygen. In case where it is impossible blank burn at 1100 to 1200°C. In the case where many number of those are blank burned at once, after cooling, without coating grease or the like preserve in a desiccator, deal with pincet or the like and do not touch with hand directly. Because those preserved for a long time have a fear that the blank test value has become high, carry out again the blank burning.

- (2) High Frequency Porcelain Combustion Crucible (hereafter referred to as the "crucible") The crucible to be used for high frequency induction heating furnace is to be FC1 or FC2 and the receiving stand, FCB1 of JIS R 1308. As required, the crucible is applied with a lid, and the lid is to be FCC1 or FCC2 of JIS R 1308.

As to crucible, lid and receiving stand, those blank burned at the same temperature as the heating temperature of sample while feeding air or oxygen preliminarily should preferably be used, but if it is impossible, blank burn at 1100 to 1200°C. In the case where many of those are burned at once, after cooling, preserve in a desiccator without coating grease or the like, deal with pincet or the like, and do not touch with hand directly. Because those preserved for a long period have a fear that the blank test value has become high, carry out blank burning again.

- (3) Decomposition Auxiliary The decomposition auxiliary is used by preliminarily mixing with sample or placing on the sample in order to make easy the generation of sulfur in the sample as sulfur dioxide, and the following matters of (a) to (d) are used independently or in combustion of two or three classes. In either cases, the sulfur content should preferably be low as far as possible.

- (a) Iron For example, granular 149 to 1000 μm
 (b) Tin For example, granular 250 to 1000 μm
 (c) Tungsten For example, granular 250 to 1000 μm
 (d) Tungsten trioxide Powder state

4.5 Weighing-out Quantity of Sample and Adding Quantity of Decomposition Auxiliary The weighing-out quantity of sample and adding quantity of decomposition auxiliary shall be in accordance with either one of the following.

- (1) In the Case of Using Tubular Electric Resistance Heating Furnace Weigh out the sample quantity, corresponding to sulfur content, and according to Table 1 to the nearest 0.1 mg.

In the case of using nitrogen for carrier gas, according to Table 1, use tungsten trioxide (WO_3) [4.4 (3) (d)] as decomposition auxiliary by mixing with sample thoroughly.

In the case of using oxygen for carrier gas, as a rule, do not use decomposition auxiliary.

Table 1. Weighing-out Quantity of Sample and Adding Quantity of Decomposition Auxiliary

Sulfur content wt %	Weighing-out quantity of sample g	Adding quantity of decomposition auxiliary (WO_3)g
0.005 or over to and excluding 0.05	1.00	1.0
0.05 or over to and excluding 0.3	0.50	0.5
0.3 or over to and excluding 1	0.20	0.2
1 min.	0.10	0.1

- (2) In the Case of Using High-frequency Induction Heating Furnace Weigh-out the sample quantity corresponding to sulfur content, as a rule, according to Table 1 to the nearest 0.1 mg, and add decomposition auxiliary [4.4 (3)]. Add the decomposition auxiliary of quantity most suitable for the weighing out quantity of sample and combustion apparatus to mix thoroughly or cover on the sample.