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JAPANESE INDUSTRIAL STANDARD

General rules for determination of hydrogen in metallic materials

JIS Z 2614—1990

Translated and Published

by

Japanese Standards Association

Printed in Japan

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the original Standard in Japanese is to be final authority.

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General rules for determination of hydrogen in metallic materials

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1. Scope

This Japanese Industrial Standard specifies the following general matters in determination method of hydrogen in metallic materials.

- (1) Method
- (2) Apparatus
- (3) Sampling and preparation of sample
- (4) Operation
- (5) Arrangement of results
- (6) Other matters

Remark: The units and numerical values given in { } in this Standard are in accordance with the International System of Units (SI) and, appended for informative reference.

Further, in this Standard the traditional units and the numerical values and the units according to SI and the converted value based on them in the { } thereafter are exchanged to the units and numerical values shown in { } on and after January 1, 1991.

2. Method

This method is the method to determine by separating the hydrogen from other coexisting gases by heating or heat melting metallic sample in vacuum or inert gas flow and by extracting hydrogen in sample and is shown as follows.

2.1 Gas Extraction Method

- (a) High-temperature Vacuum Melting Method Melt the sample in vacuum in a graphite crucible, and extract the hydrogen together with other gases.
- (b) Low-temperature Vacuum Melting Method In vacuum add tin as flux in a refractories crucible such as quartz to the sample, melt at a temperature not higher than the melting point of sample, and extract hydrogen together with other gases.
- (c) Vacuum Heating Method In vacuum heat the sample at a temperature not higher than the melting point under the solid condition as it is to extract hydrogen together with other gases.

Informative reference: There are a high temperature method and a low temperature method.

- (d) Inert-gas Fusion Method Fuse the sample in a graphite crucible in an inert-gas flow, and discharge hydrogen together with other gases.
- (e) Inert-gas Heating Method Heat the sample at a temperature not higher than the melting point under the solid condition as it is in an inert-gas flow, and discharge hydrogen together with other gases.

2.2 Gas Analysis Method

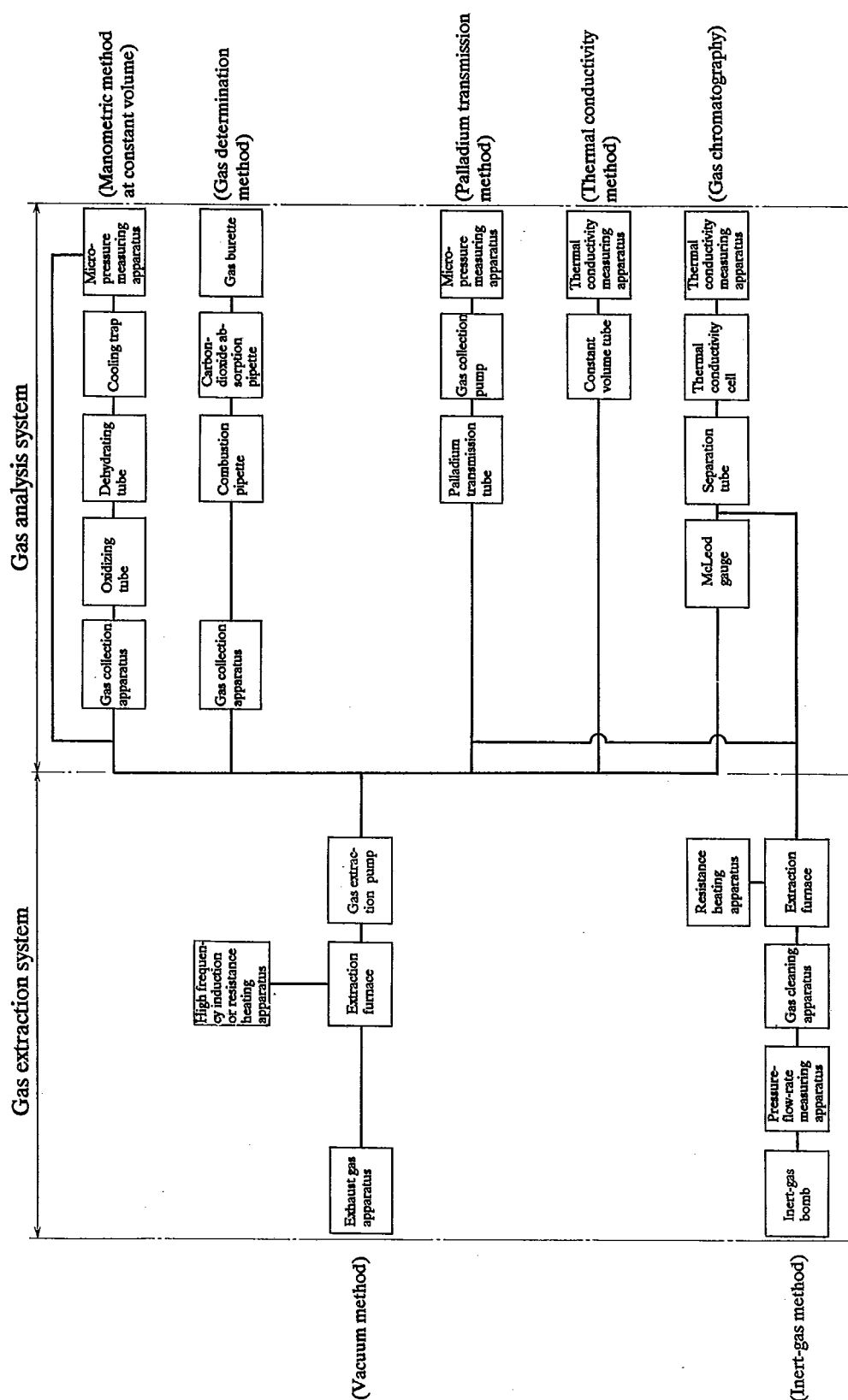
- (a) Manometric Method at Constant Volume Collect the gas extracted from the sample into a vacuum container of a definite volume to measure the pressure, remove the water generated by passing through oxidizing agent and dehydrating agent, again measure the pressure and calculate the hydrogen amount.

- (b) Gas Volumetric Method Together with collection of gas extracted from the sample, add oxygen, burn with a microgas analysis apparatus connected with burning pipette, absorption pipette, and gas burette to absorb and calculate the hydrogen amount from oxygen consumption amount.
- (c) Palladium Transmission Method Feed the gas extracted from the sample into a heated palladium tube, collect the transmitted hydrogen to measure the pressure, and calculate the hydrogen amount.
- (d) Thermal Conductivity Method Collect the gas extracted from the sample into a definite volume containing a thermal conductivity cell, measure the change of thermal conductivity due to hydrogen, and calculate the hydrogen amount.
- (e) Gas Chromatography Collect the gas extracted from the sample into a definite volume, introduce together with the carrier gas such as argon into a thermal conductivity cell through an absorption type separating tube, measure the change of thermal conductivity due to hydrogen, and calculate the hydrogen amount.

3. Apparatus

3.1 Constitution of Apparatus The analytical apparatus to be used usually shall consist of gas extraction system, gas analytical system and others, and according to the method each unit apparatus in connected to be consisted. An example of constitution of apparatus is shown in Fig. 1.

Fig. 1. Example of Constitution of Apparatus



3.2 Gas Extraction System

3.2.1 Vacuum Fusion Method The vacuum fusion method shall be as follows:

(1) Materials and Reagents

- (a) Graphite crucible and graphite funnel
- (b) Graphite powder 74 to 44 μm (corresponding to 200 to 325 mesh)
- (c) Wax for high vacuum
- (d) Grease for vacuum

(2) Apparatus The gas extraction system consists of high frequency induction heating apparatus, extraction furnace, gas extraction pump, exhaust gas apparatus, etc.

- (a) High Frequency Induction Heating Apparatus The high frequency induction heating apparatus is to be able to keep the crucible, sample, etc. in the extraction furnace at a temperature not lower than the degasing temperature and consists of high frequency power source and heating coil.
- (b) Extraction Furnace Allow the furnace tube to be made of hard glass, put the graphite crucible outer tube and inner tube and graphite funnel thereinto and fix the quartz cylinder filled with graphite powders or molybdenum cylinder put-into with quartz crucible. Allow fixing of them to be hanging down method (Figs. 2 and 3) and the method to support with furnace-tube bottom-part furnace plug (Fig. 4). At the upper part of furnace tube, provide the prism for temperature measurement, temperature measurement window, sample injection opening, gas transfer tube, etc. Let the cooling of furnace tube be the method to carry out with water (Fig. 3) and the method to carry out with a blower (Figs. 2 and 4).
- (c) Gas Extraction Pump The pump having the purpose to extract gas from the sample and a mercury diffusion pump of high exhaust gas speed, or the like is used.
- (d) Exhaust-gas Apparatus The apparatus having the purpose to exhaust gas in the apparatus to vacuum, and connected with a mercury diffusion pump or the like and oil hydraulic rotary pump.

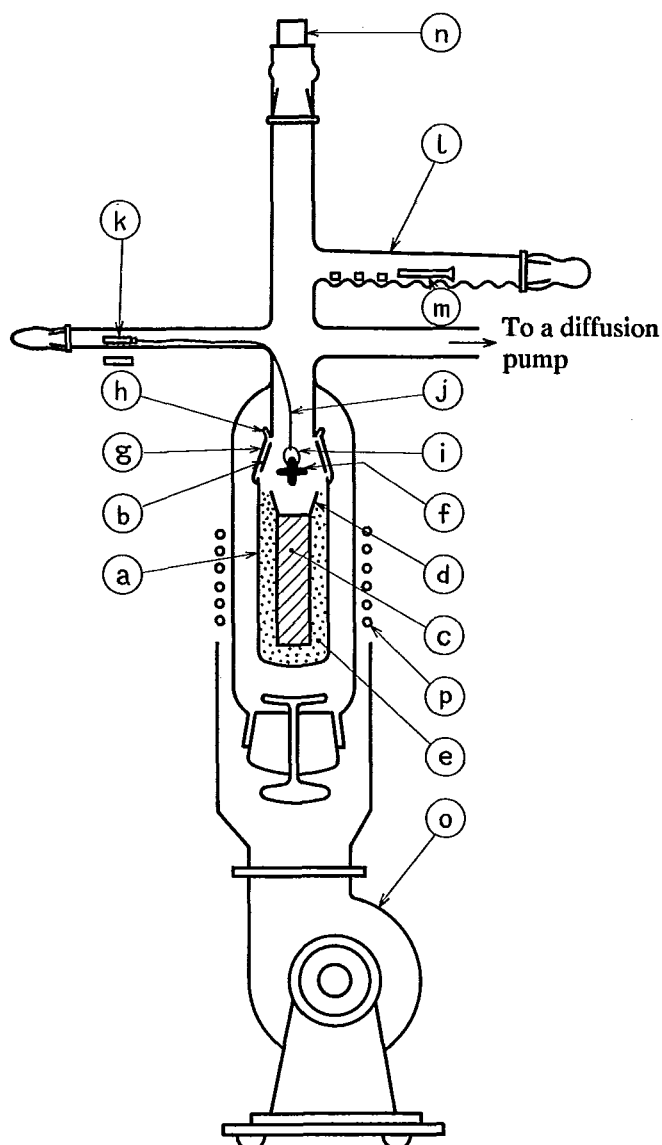
(3) Assembling of Crucibles

(3-1) In the Case of Using a Graphite Crucible

- (a) Fill graphite powder into a quartz cylinder up to the height of 30 to 35 mm from the bottom. In the case of making the graphite crucibles double (Fig. 4), preliminarily lap them, and place highly on the graphite powder so as to be same axis as that of quartz cylinder.
- (b) Place a lid of cone shape on the graphite crucible so as the graphite powder not to enter into the graphite crucible, and gently add graphite powder between the graphite crucible and the quartz cylinder up to the approximately upper end of graphite crucible.
- (c) Detach the conical-shape lid, attach it to graphite funnel, place the lid of conical shape on it and add graphite powder up to the upper end of graphite funnel. Insert a copper wire of approximately 1 mm in diameter into graphite powder, rotate it once around the graphite crucible to extinguish voids of graphite powder. Add the insufficient content and remove the conical-shape lid.
- (d) Fit the quartz cylinder entered with a graphite crucible with a furnace plug (Figs. 2 and 4), insert from under part of furnace tube and seal the ground joint part with furnace plug with the wax for high vacuum.

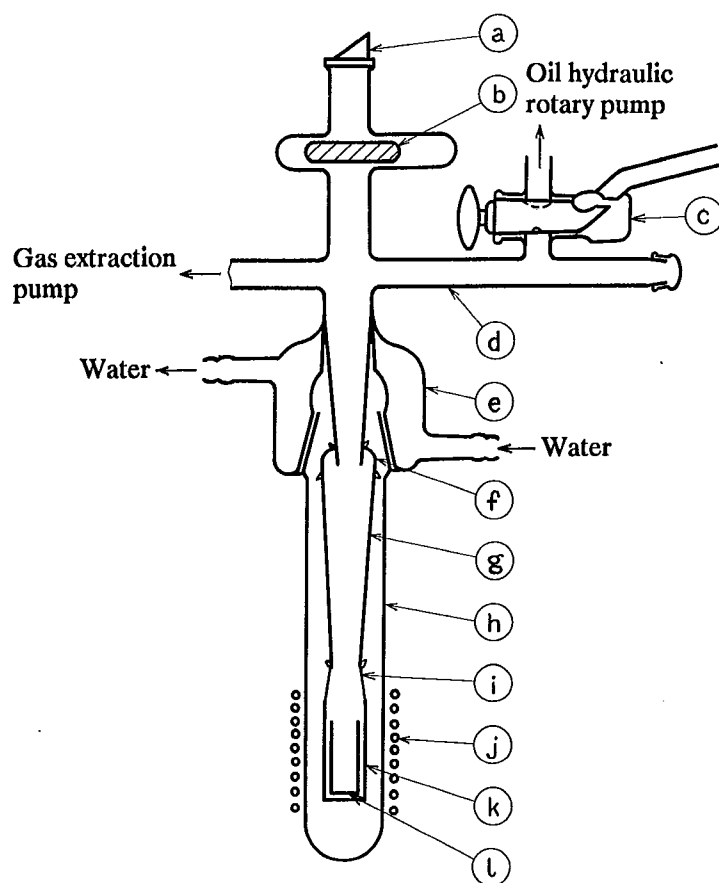
(3-2) In the Case of Using a Quartz Crucible Hang down the molybdenum cylinder containing a quartz crucible entered with bath metal (Fig. 3) and connect the furnace tube.

Fig. 2. Example of Extraction Furnace



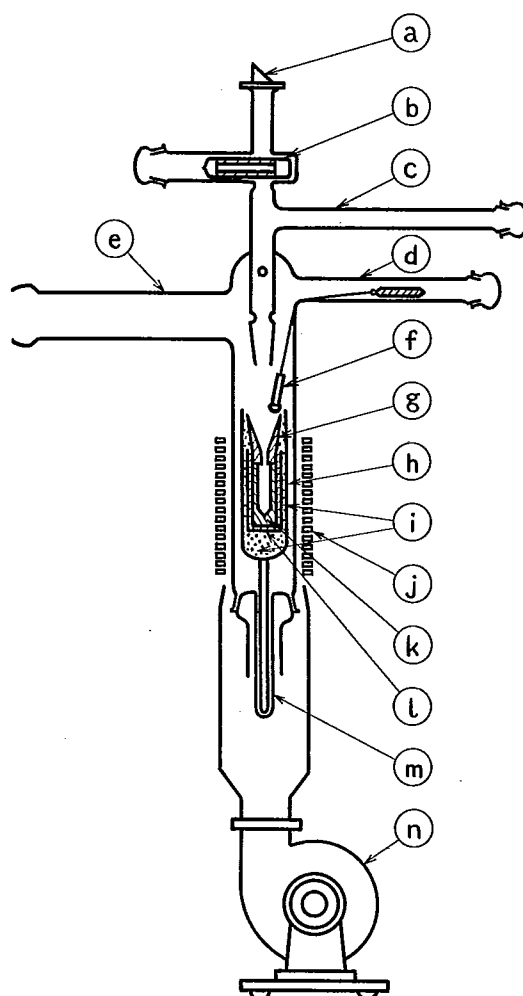
a	Quartz cylinder
b	Quartz heat shielding cylinder
c	Graphite crucible
d	Graphite funnel
e	Graphite powder
f	Graphite plug
g	Platinum wire
h	Glass hook
i	Tantalum wire
j	Molybdenum wire
k	Soft iron bar
l	Side tube for filling sample
m	Iron bar for projection of sample
n	Right angular prism for temperature measurement
o	Blower
p	Heating coil

Fig. 3. Example of Extraction Furnace



a	Right angular prism made of quartz for temperature measurement
b	Shutter
c	Double cock
d	Side tube for filling of sample
e	Water cooling tube
f	Platinum wire
g	Quartz-sample guide tube
h	Transparent quartz furnace tube
i	Molybdenum wire
j	Heating coil
k	Molybdenum cylinder
l	Quartz crucible

Fig. 4. Example of Extraction Furnace



a	Quartz right angular prism for temperature measurement
b	Shutter
c	Side tube for filling of sample
d	Side tube for opening-and-closing of graphite plug
e	Gas transfer tube
f	Graphite plug
g	Graphite funnel
h	Quartz cylinder
i	Graphite powder
j	High frequency heating coil
k	Inside graphite crucible
l	Outside graphite crucible
m	Furnace-tube bottom-part furnace plug
n	Blower

3.2.2 Vacuum Heating Method The vacuum heating method shall be as follows.

(1) Material and Reagent

Grease for vacuum

(2) Apparatus The gas extraction system consists of a heating apparatus, extraction furnace, gas-extraction pump, exhaust gas apparatus, etc.

(a) Heating Apparatus The heating apparatus is to be able to maintain the extraction furnace at a temperature not lower than degassing temperature. As to the heating apparatus, generally resistance heating system is used, and to the rapid analysis of small type sample, high frequency induction heating system may be used.

(b) Extraction Furnace Use a furnace tube (Fig. 5) of which one end of quartz tube of 25 to 40 mm in inner diameter and 300 to 400 mm in length is sealed and of which other end is ground joint with water cooling type glass cap and connect the water cooling cap with the extraction pump.

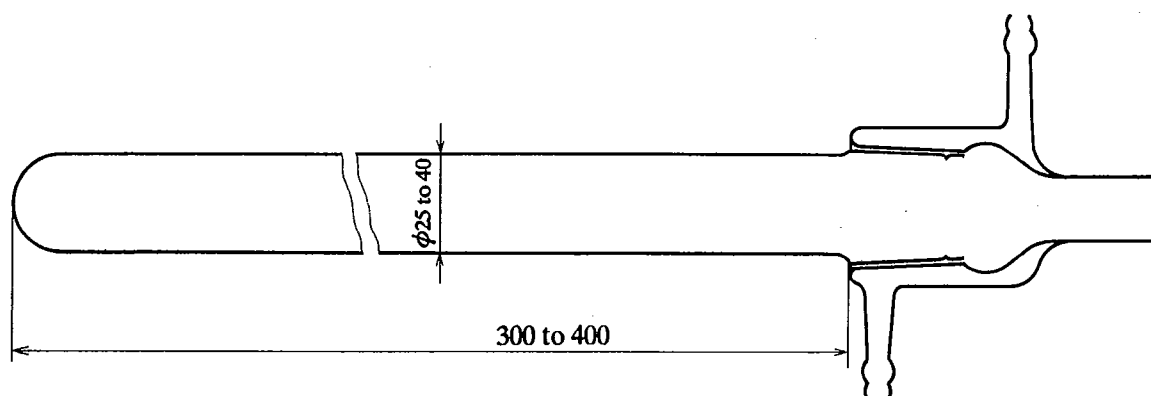
Informative reference: There are vertical type and lateral type and the lateral type is convenient for use.

(c) Gas Extraction Pump The gas extraction pump is to be in accordance with the case of 3.2.1 (2) (c) vacuum fusion method, as appropriate.

(d) Exhaust-gas Apparatus The exhaust-gas apparatus is to be in accordance with 3.2.1 (2) (d).

Fig. 5. Example of Vacuum Heating Method Furnace Tube

Unit: mm



3.2.3 Inert-gas Heating Method The inert-gas heating method shall be as follows.

(1) Material and Reagent

- (a) Inert gas Argon (it is preferable to be 99.999 % or more) or helium (it is preferable to be 99.99 % or more).
- (b) Denitrification-deoxydation agent Sponge titanium or the like.
- (c) Dehydrating agent Phosphorus pentaoxide or the like.

(2) Apparatus The gas extraction system consists of a heating apparatus, extraction furnace, inert gas cleaning apparatus, etc.

- (a) Heating Apparatus The heating apparatus is to be able to maintain the extraction furnace at a temperature not lower than the degassing temperature. For heating apparatus, generally the resistance heating system is used.
- (b) Extraction Furnace Its furnace tube is 25 to 40 mm in inner diameter and 400 to 600 mm in length and it is to be provided with a quartz furnace tube having inert-gas introduction opening and sample injection opening. The ground joint part is cooled with water, as required.
- (c) Inert-gas Cleaning Apparatus The inert-gas cleaning apparatus has the object to remove nitrogen, oxygen, moisture, etc. in used inert gas, and is connected with a tube filled with denitrification-deoxidation agent, a small type electric furnace for heating it at approximately 500°C and a tube filled with dehydrating agent. However, in the case of using argon of not less than 99.999 %, the denitrification-deoxidation agent tube may be omitted.

3.3 Gas Analysis System

3.3.1 Manometric Method at Constant Volume The manometric method at constant volume shall be as follows.

(1) Material and Reagent

- (a) Oxidizing agent, copper oxide, etc.
- (b) Dehydrating agent, phosphorus pentaoxide, etc.
- (c) Silicone oil

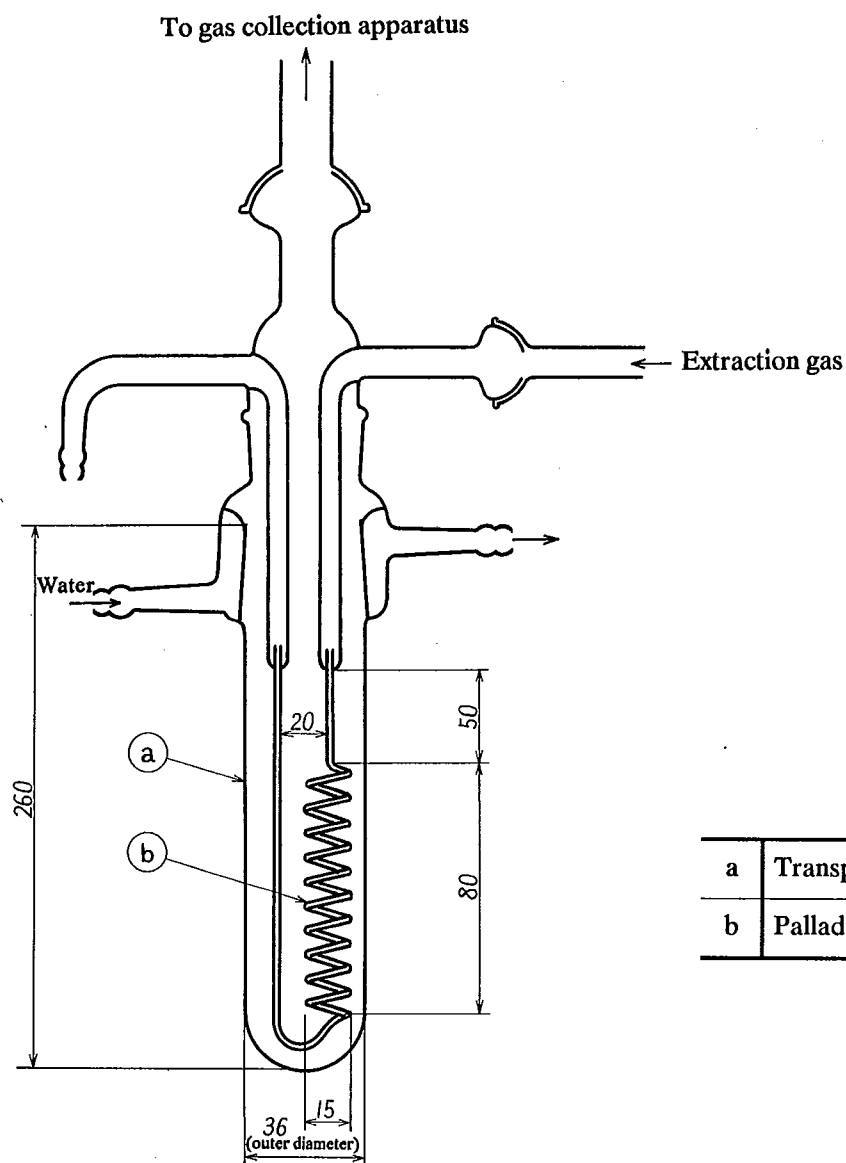
- (2) Apparatus The gas analysis system consists of a gas collection apparatus, oxidizing apparatus for collected gas, dehydrating tube, micro-pressure measuring apparatus, etc.
- (a) Gas Collection Apparatus The gas collection apparatus capable of collecting the gas extracted from the sample into a definite volume gas reservoir by using a mercury ejector pump (combined with gas circulation) of high back pressure characteristic.
- (b) Oxidizing Apparatus The oxidizing apparatus having the purpose to make the collected hydrogen, carbon monoxide, respectively water, carbon dioxide, and provided with a tube filled with oxidizing agent and a small type electric furnace for heating it.
- (c) Dehydrating Tube A tube filled with dehydrating agent for absorbing the generated water.
- (d) Micro-pressure Measuring Apparatus The apparatus for measuring micro-pressure at each step of collection and dehydrating and oil hydraulic manometer or McLeod gauge is used.

3.3.2 Palladium Transmission Method The palladium transmission method shall be as follows.

- (1) Material and Reagent
Silicone oil
- (2) Apparatus The gas analysis system consists of a palladium transmission apparatus, gas collection apparatus, micro-pressure measuring apparatus, etc.
- (a) Palladium Transmission Apparatus (Figs. 6 and 7) The apparatus provided with a palladium tube of approximately 0.2 mm in wall thickness, 1 to 10 mm in outer diameter, and 50 to 1000 mm in length, and a resistance heating furnace for heating this.
- (b) Gas Collection Apparatus A mercury diffusion pump of high back pressure characteristic or the like is used. In the case where a mercury manometer is used as the micro-pressure measuring apparatus, further a Toepler pump is to be provided.
- (c) Micro-pressure Measuring Apparatus An oil hydraulic manometer or McLeod gauge is used. A mercury manometer can be used, also.

Fig. 6. Example of Palladium Heating Tube for Inert Gas

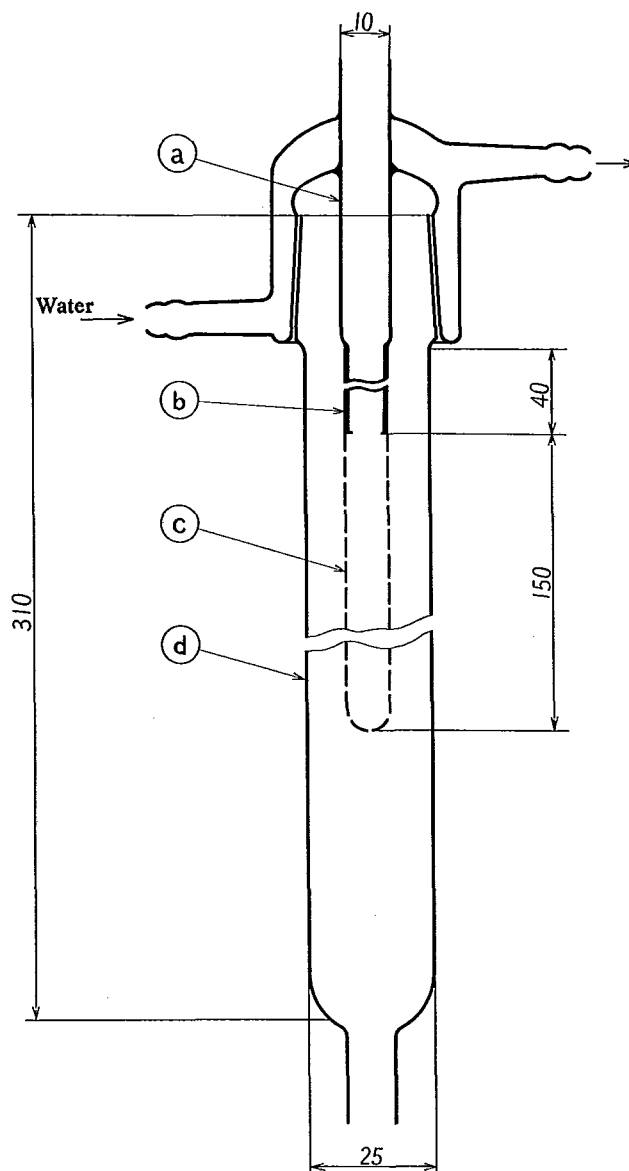
Unit: mm



a	Transparent quartz tube
b	Palladium tube

Fig. 7. Example of Palladium Heating Tube for Vacuum Heating

Unit: mm



a	Glass tube
b	Platinum tube
c	Palladium tube (8 mm in outer diameter, 0.2 mm in wall thickness)
d	Transparent quartz tube

3.3.3 Gas Volumetric Method The gas volumetric method shall be as follows.

(1) Material and Reagent

Potassium hydroxide solution (33 %)

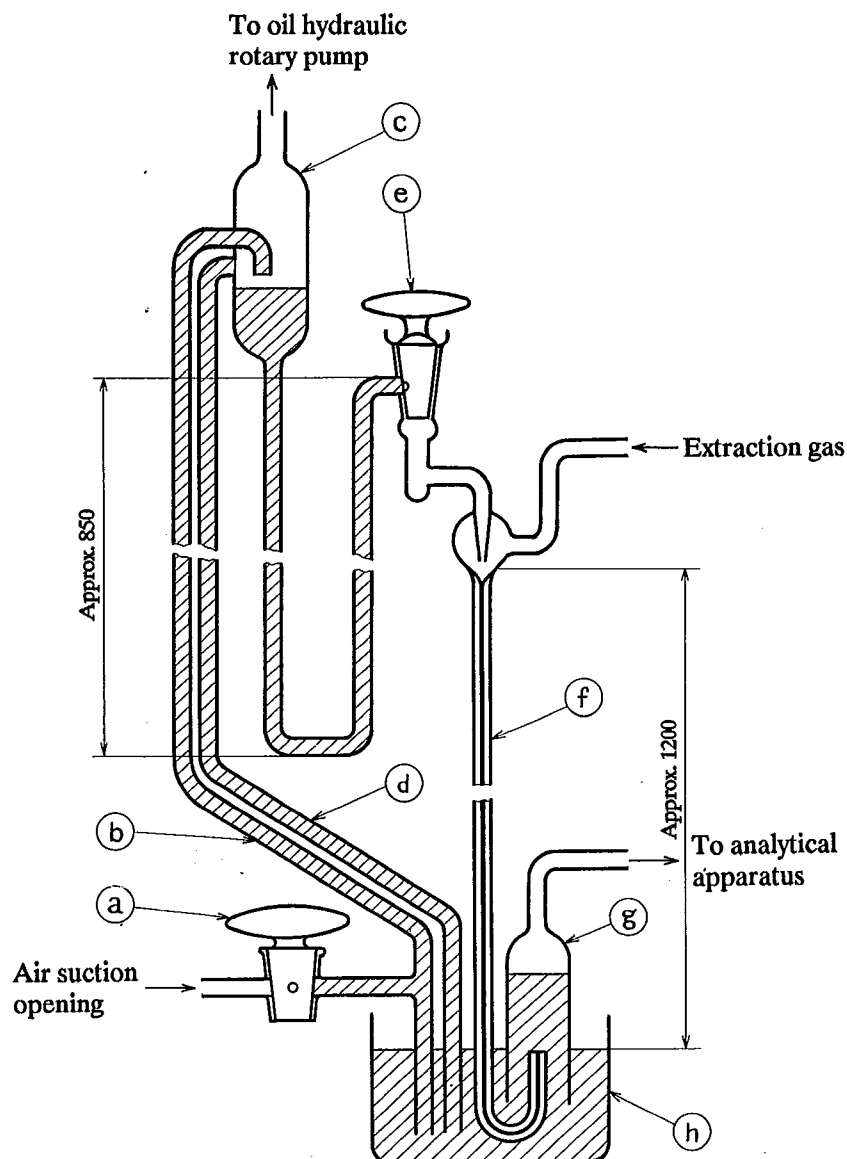
(2) Apparatus The gas analysis system consists of a gas collection apparatus, gas analysis apparatus, etc.

(a) Gas Collection Apparatus The gas collection apparatus consists of the collection pump such as mercury dropping pump or the like and gas reservoir.

(a-1) Mercury Dropping Pump (Fig. 8) The mercury dropping pump is used for collecting the extracted gas and to return to the ordinary pressure. The mercury in the mercury reservoir together with the air to be sucked up through adjusting cock into an air separating chamber, the air is exhausted with an oil hydraulic rotary pump, and the mercury is dropped down into a mercury dropping-down capillary through a dropping amount adjusting cock. The capillary is 1.8 to 2.2 mm in inner diameter and in order to increase the gas exhausting speed two or three pieces in parallel may be used.

Fig. 8. Example of Mercury Dropping-down Pump

Unit: mm



a	Air-suction-amount adjusting cock	e	Mercury-dropping-down-amount adjusting cock
b	Mercury sucking up tube	f	Mercury-dropping-down capillary
c	Air separating chamber	g	Gas reservoir
d	Mercury spilling-out tube	h	Mercury reservoir

(a-2) **Gas Reservoir** The gas reservoir has the purpose to collect the gas dropped down together with mercury from the mercury-dropping-down capillary, and the upper end of glass tube immersed in the mercury bath is connected with the analytical apparatus.

(b) **Gas Analytical Apparatus** The gas analytical apparatus is for analysis of collected gas, and consists of gas burette, explosion pipette, or combustion pipette, carbon dioxide absorption pipette, oxygen generating apparatus, etc.