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**General rules for determination of oxygen
in metallic materials**

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Foreword

This Japanese Industrial Standard has been revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by The Japan Society for Analytical Chemistry (JSAC)/Japanese Standards Association (JSA) with a draft being attached, based on the provision of Article 12, paragraph (1) of the Industrial Standardization Act applied mutatis mutandis pursuant to the provision of Article 16 of the said Act. This edition replaces the previous edition (**JIS Z 2613** : 2006), which has been technically revised.

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General rules for determination of oxygen in metallic materials

1 Scope

This Japanese Industrial Standard specifies common general matters concerning the methods for determination of oxygen in metallic materials.

A list of technically significant revisions from the previous edition with reasons is given in Annex A.

2 Normative references

Part or all of the provisions of the following standards, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

- JIS K 0050 *General rules for chemical analysis*
- JIS K 0113 *General rules for methods of potentiometric, amperometric, coulometric, and Karl Fischer titrations*
- JIS K 0117 *General rules for infrared spectrophotometric analysis*
- JIS K 0211 *Technical terms for analytical chemistry (General part)*
- JIS K 0212 *Technical terms for analytical chemistry (optical part)*
- JIS K 0213 *Technical terms for analytical chemistry (Electrochemistry part)*
- JIS K 0215 *Technical terms for analytical chemistry (Analytical instrument part)*
- JIS R 6010 *Coated abrasive grain sizes*
- JIS Z 8402-1 *Accuracy (trueness and precision) of measurement methods and results — Part 1 : General principles and definitions*
- JIS Z 8402-2 *Accuracy (trueness and precision) of measurement methods and results — Part 2 : Basic method for the determination of repeatability and reproducibility of a standard measurement method*
- JIS Z 8402-3 *Accuracy (trueness and precision) of measurement methods and results — Part 3 : Intermediate measures of the precision of a standard measurement method*
- JIS Z 8402-4 *Accuracy (trueness and precision) of measurement methods and results — Part 4 : Basic methods for the determination of the trueness of a standard measurement method*
- JIS Z 8402-5 *Accuracy (trueness and precision) of measurement methods and results — Part 5 : Alternative methods for the determination of the precision of a standard measurement method*

JIS Z 8402-6 *Accuracy (trueness and precision) of measurement methods and results — Part 6 : Use in practice of accuracy values*

3 Terms and definitions

For the purpose of this Standard, the terms and definitions given in **JIS K 0050**, **JIS K 0211**, **JIS K 0212**, **JIS K 0213** and **JIS K 0215**, and the following apply.

3.1

gas extraction

operation of generating carbon monoxide by making oxygen which forms oxides and/or oxygen dissolved in solid-solution contained in a metal sample react with carbon of a graphite crucible and of discharging it from a melted metal sample

Note to entry 1 Although carbon dioxide may also be generated inside the graphite crucible depending on a sample, the amount of carbon dioxide generated is small enough to be disregarded in the metal sample.

Note to entry 2 The discharged gas is called extracted gas.

3.2

gas extracting temperature

temperature set under the condition that gas extraction is performed

3.3

degassing

operation of expelling gas components in a crucible and/or bath metals put in a crucible by pre-burning a graphite crucible at the temperature set at gas extracting temperature or higher

3.4

impulse heating

heating method in which a graphite crucible is directly energized and the temperature of the crucible is raised to 2 000 °C or higher in a few seconds

3.5

impulse furnace

furnace constituted of a fixed upper water-cooled copper electrode and a lower water-cooled copper electrode which can move up and down, in which it is possible to perform the impulse heating of a graphite crucible inserted between both electrodes

Note to entry 1 It is also called electrode furnace.

3.6

specimen

solidified sample taken from molten metal and sample cut out from block, plate, foil, tube, wire, etc. brought in a laboratory

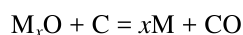
4 General matters

The common matters for determination method shall be as follows.

- a) General matters common to chemical analysis shall be as specified in **JIS K 0050**.
- b) General matters common to infrared absorption method shall be as specified in **JIS K 0117**.
- c) General matters common to coulometric method shall be as specified in **JIS K 0113**.
- d) Water in which dissolved oxygen is removed shall be prepared for analysis as specified in **E.1** of **JIS K 0050** at every use.
- e) The reagent specified in Japanese Industrial Standards (**JISs**) or that at least equivalent to this shall be used. When there is no applicable **JIS**, that which does not interfere with analysis shall be used.
- f) The apparatus and instruments satisfying the specified functions shall be used.
- g) Unless otherwise described, the component concentration in metal shall be expressed by mass fraction.

5 Classification of determination methods

The metal sample is put into a graphite crucible in inert gas flow and heated to be fused and the oxygen in the sample is determined by extracting it as carbon monoxide. In this method, the metal oxide reacts with carbon as shown in the following formula and generates carbon monoxide.



In this case, nitrogen, hydrogen, methane, etc. are likely to be included in this extracted gas, and therefore, the carbon monoxide is separated from those gases and determined to calculate the amount of oxygen.

The oxygen determination shall be performed by either of the following two methods.

- a) **Infrared absorption method** The infrared absorption method is a method in which the extracted gas is transferred to an infrared absorption detector, the change of the amount of infrared absorption of carbon monoxide is measured and the amount of oxygen is calculated ¹⁾, or a method in which after oxidizing carbon monoxide to carbon dioxide, carbon dioxide is transferred to an infrared absorption detector, the change of the amount of infrared absorption of carbon dioxide is measured and the amount of oxygen is calculated.

In an apparatus with a mechanism in which carbon monoxide is oxidized to carbon dioxide and measurement is performed, when a sample with high hydrogen concentration (for example, not less than 0.1 %) is measured, generated methane gas is converted into carbon dioxide and water in an oxidation tube [tube in which heated copper (II) oxide is filled] and a positive error is caused in the value of amount of oxygen. When measuring such a sample, methane gas shall be removed or measurement shall be performed with carbon monoxide as it is without passing

through the oxidation tube.

Note ¹⁾ There is also an apparatus with measurement and correction functions of carbon dioxide.

- b) **Coulometric method** The coulometric method is a method in which the extracted gas is oxidized with an oxidizing agent, this is introduced into weak alkaline barium perchlorate solution, the increment of hydrogen ion concentration due to absorption of carbon dioxide is neutralized by electrolysis and the amount of oxygen is calculated from the quantity of electricity.

6 Apparatus

6.1 Composition of apparatus

The analytical instrument to be used consists of a gas extracting system (inert gas fusion method) and gas analysing system (infrared absorption method or coulometric method) by connecting each unit apparatus according to the test method.

6.2 Gas extracting system

The gas extracting system shall be as follows.

- a) **Materials and reagents** The main materials and reagents shall be as follows.
- 1) **Inert gas** Helium (a volume fraction of not less than 99.995 % is recommended) or argon (a volume fraction of not less than 99.999 % such as Class 1 of **JIS K 1105** is recommended)
 - 2) **Deoxidant** Copper, etc.
 - 3) **Organic gas decomposing agent** Copper (II) oxide, etc.
 - 4) **Carbon dioxide absorbent** Silica gel impregnated with sodium hydroxide, etc.
 - 5) **Dehydrating agent** Magnesium perchlorate, etc.
 - 6) **Graphite crucible** The graphite crucible shall be suitable for the furnace to be used and shall have a low blank value of oxygen. A graphite crucible shall be handled using metal graphite crucible scissors.

NOTE 1 Examples of the type of graphite crucibles are a single crucible, double crucible and high temperature crucible.
 - 7) **Graphite funnel** The graphite funnel shall be used when required. It shall be suitable for the apparatus to be used and shall have a low blank value of oxygen.
 - 8) **Graphite powder** The graphite powder shall have a particle size of 74 µm to 147 µm and a low blank value of oxygen.
 - 9) **Bath metals** The bath metals shall be metals such as nickel, tin, platinum, copper and iron and shall have a low blank value of oxygen.

NOTE 2 Metals such as nickel, tin, platinum, copper and iron are commercially available in the form of capsule, pellet, basket, grain, foil, etc.
- b) **Apparatus** The apparatus consists of an inert gas purifying part, gas extracting

part, etc. (see Figure 1).

- 1) **Inert gas purifying part** The inert gas purifying part is a part aiming at removing impurities (oxygen, organic gas, carbon dioxide, moisture, etc.) in the inert gas to be used, and normally, consists of a tube in which a deoxidant and organic gas decomposing agent are filled, a tube in which a carbon dioxide absorbent and dehydrating agent are filled, etc. heated at 400 °C to 700 °C in an electric resistance heating furnace. Other apparatuses recommended (specified) by the apparatus manufacturer may be used.

The inert gas purifying part may be omitted when, for example, the high-purity inert gas of a volume fraction of not less than 99.999 % is used or low-concentration oxygen is not determined.

- 2) **Gas extracting part** The gas extracting part is capable of extracting oxygen in the sample as carbon monoxide in the inert gas flow and has the function of air mixing prevention, degassing of a graphite crucible, etc. by which a blank value can be reduced in determination. Examples of a heating system are impulse heating and high frequency induction heating shown below.

2.1) Impulse heating system

- 2.1.1) **Heating apparatus** An impulse furnace shall be used.

- 2.1.2) **Extracting furnace** The extracting furnace is equipped with a sample charger which can charge a sample into an impulse furnace in an inert gas atmosphere. An example of an impulse heating extracting furnace is shown in Figure 2.

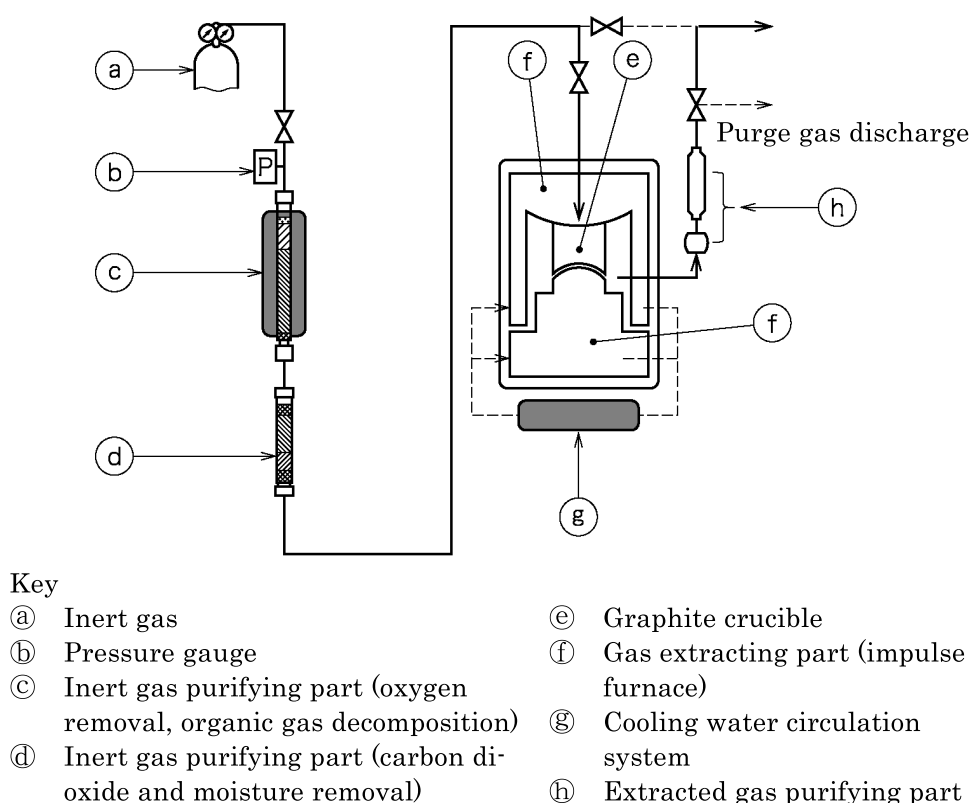
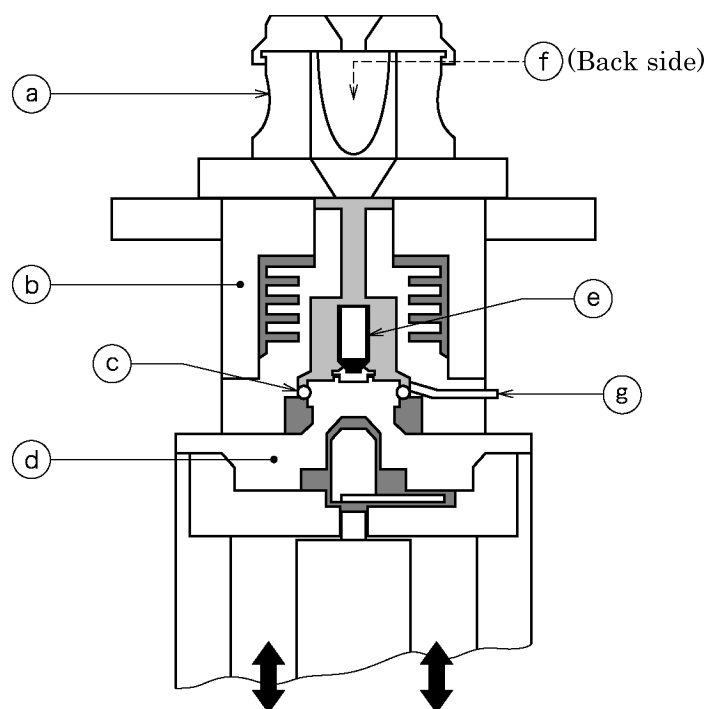


Figure 1 Example of inert gas fusion extractor composition



Key

- | | |
|---|-----------------------------|
| ① Sample charger | ⑤ Graphite crucible |
| ② Water-cooled upper electrode (fixed type) | ⑥ Inert gas inlet port |
| ③ O ring for insulation | ⑦ Extracted gas outlet port |
| ④ Water-cooled lower electrode (movable type) | |

Figure 2 Example of impulse heating extracting furnace

2.2) High frequency induction heating system

2.2.1) Heating apparatus The heating apparatus is capable of holding the graphite crucible installed in the quartz glass outside cylinder at not less than degassing temperature, and consists of a high frequency power source and heating coil.

2.2.2) Extracting furnace An example of a high frequency induction heating extracting furnace is shown in Figure 3. The furnace cylinder consists of a lower furnace cylinder (⑥) and upper cap (① to ⑤). The lower furnace cylinder is made of quartz glass. A graphite crucible is put into the quartz glass outside cylinder in the lower furnace cylinder, and graphite powder is filled in the surrounding. The upper cap is made of hard glass and is equipped with the prism or reflector for measuring temperature with an optical pyrometer, the temperature detecting window, the sample charging inlet port, etc.

2.2.3) Assembly of graphite crucibles

2.2.3.1) Fill graphite powder into the quartz glass outside cylinder up to the height of 20 mm to 30 mm from the bottom and put a graphite crucible in the centre

on the top of this.

- 2.2.3.2) While taking care to ensure that the graphite powder does not enter into the graphite crucible, fill the graphite powder lightly up to the almost top end of the graphite crucible between the graphite crucible and the quartz glass outside cylinder.
- 2.2.3.3) When using a graphite funnel, attach the graphite funnel on the top of the graphite crucible and add the graphite powder by a height of 3 mm to 5 mm further.
- 2.2.3.4) Place the quartz glass outside cylinder in which the graphite crucible is put on a supporting pillar, insert it from under the furnace cylinder and hold it.

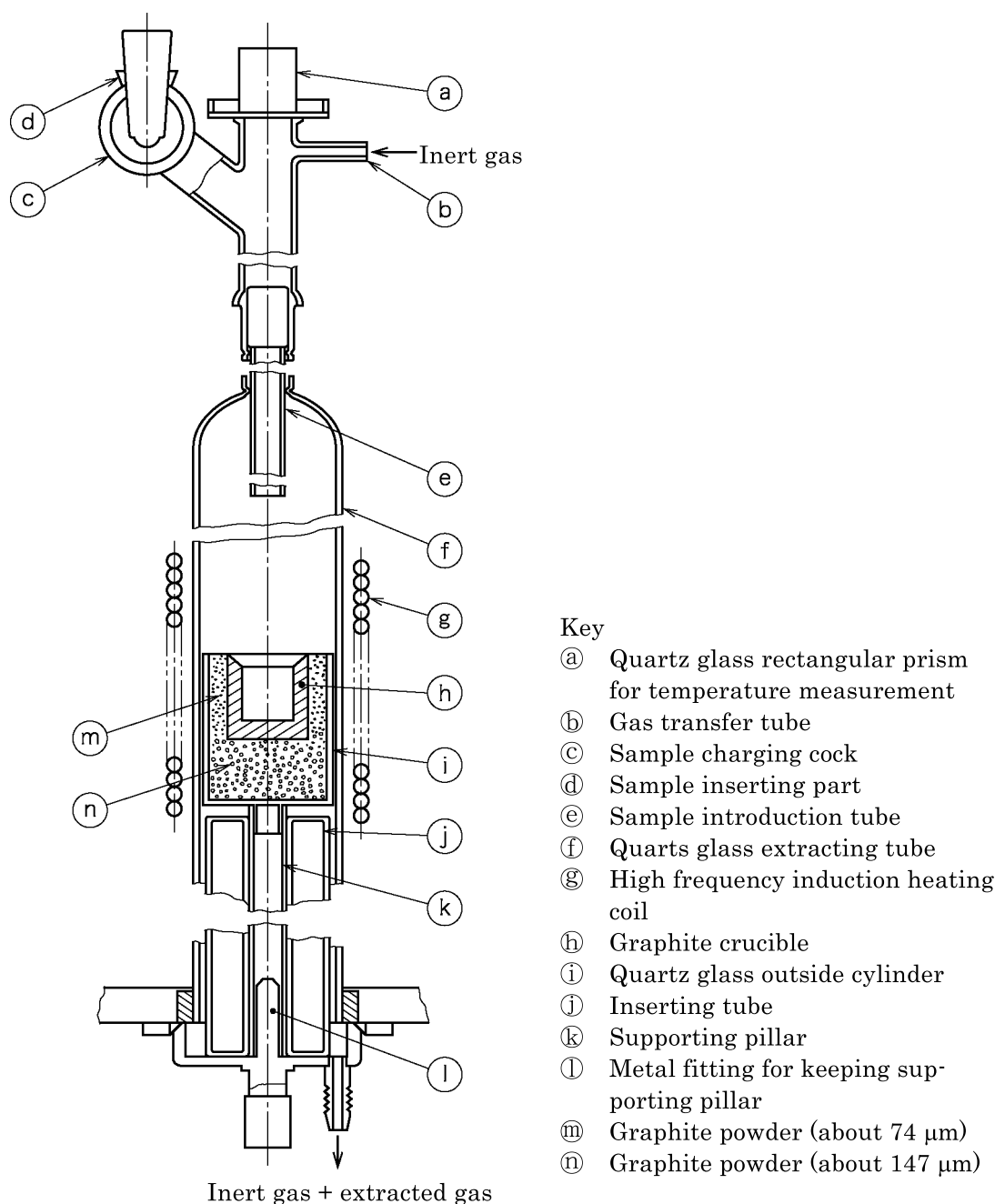


Figure 3 Example of high frequency induction heating extracting furnace

6.3 Gas analysing system

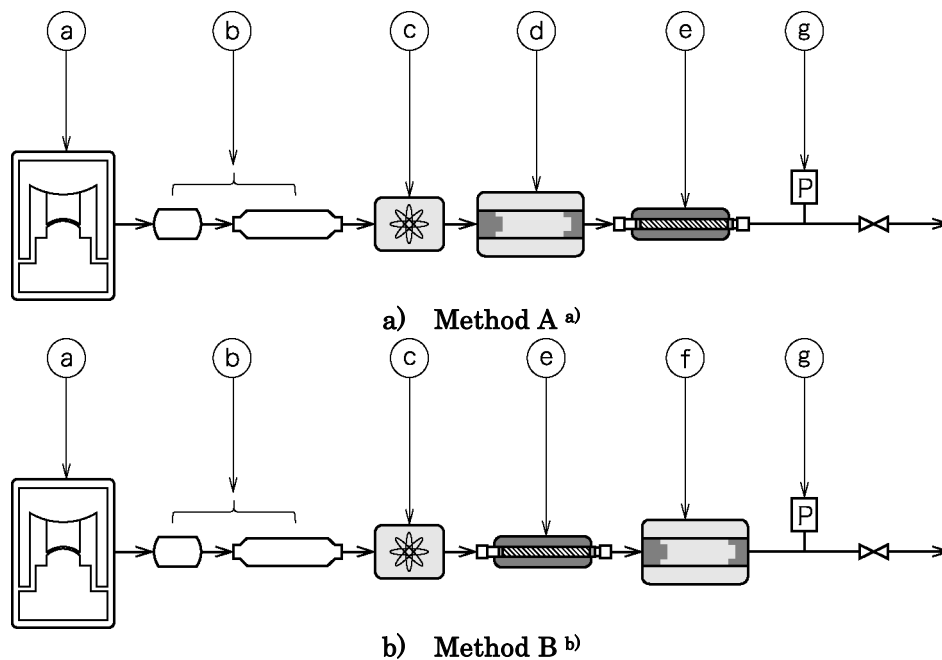
6.3.1 Infrared absorption method

There are two types of infrared absorption methods, that is, a method in which the extracted carbon monoxide is detected with an infrared absorption detector in a state as it is and a method in which carbon dioxide obtained by oxidizing the extracted carbon monoxide is detected with an infrared absorption detector. The infrared absorption methods shall be as follows (see Figure 4).

NOTE The apparatus equipped for both methods is also commercially available.

a) **Materials and reagents** The main materials and reagents shall be as follows.

- 1) **Quartz glass wool**
- 2) **Disk filter**
- 3) **Oxidizing agent** Copper (II) oxide, etc.



Key

- | | |
|---|--|
| ① Impulse furnace | ⑤ Extracted gas oxidizing part (oxidizing carbon monoxide to carbon dioxide) |
| ② Extracted gas purifying part | ⑥ Extracted gas measuring part (carbon dioxide infrared absorption detector) |
| ③ Flow rate control part | ⑦ Pressure gauge |
| ④ Extracted gas measuring part (carbon monoxide infrared absorption detector) | |

Note ^{a)} For Method A, in order to detect a small amount of carbon dioxide which is generated when oxides are measured, an apparatus in which the infrared detector of carbon dioxide is added before the extracted gas oxidizing part, an apparatus in which the catalyst (e.g. platinum on carbon) is added in order to reduce carbon dioxide to carbon monoxide, etc. are also commercially available.

In order not to discharge harmful carbon monoxide from the apparatus, the extracted gas oxidizing part should be used.

Note ^{b)} Since the molar absorptivity of carbon dioxide is larger than that of carbon monoxide, Method B is useful when trace oxygen (for example, 10 ppm or less) is measured.

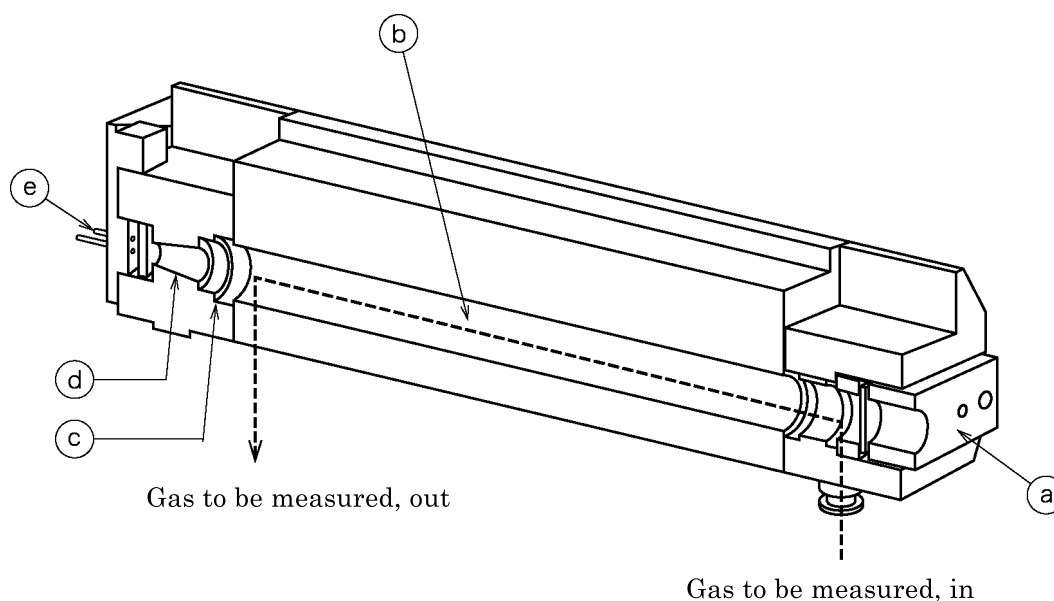
Figure 4 Example of infrared absorption measuring part composition

b) **Apparatus** The apparatus consists of an extracted gas purifying part, extracted gas oxidizing part, extracted gas measuring part, etc.

- 1) **Extracted gas purifying part** The extracted gas purifying part has the function of removing the graphite fine powder generated at the time of sample fusion, the fine powder derived from bath metals, etc. and consists of a dust collection tube in

which quartz glass wool is filled, disk filter, etc.

- 2) **Extracted gas oxidizing part** The extracted gas oxidizing part is e.g. the tube in which copper (II) oxides heated in the electric resistance heating furnace are filled, and has the function of oxidizing the carbon monoxide generated from the sample, etc. and converting it into carbon dioxide.
- 3) **Extracted gas measuring part** The extracted gas measuring part is capable of measuring the amount of infrared absorption by carbon monoxide or carbon dioxide and outputting the integrated value of the amount of absorption. An example of an infrared absorption detector is shown in Figure 5.



Key

- | | |
|-----------------------|----------------------|
| (a) Light source | (d) Energy capacitor |
| (b) Gas chamber | (e) Detector |
| (c) Wavelength filter | |

Figure 5 Example of infrared absorption detector

6.3.2 Coulometric method

The coulometric method shall be as follows.

- a) **Reagents** The main reagents shall be as follows.
 - 1) **Iodine pentoxide (granular)**
 - 2) **Sodium thiosulfate**
 - 3) **Barium carbonate (powder)**
 - 4) **Catholyte (absorbent)** Add about 50 g of barium perchlorate and 20 ml to 30 ml of 2-propanol in 1 L of water, dissolve and stir well.

- 5) **Anolyte (absorbent)** Add about 150 g to 200 g of barium perchlorate in 1 L of water, dissolve and stir well.
 - 6) **Reference liquid** Add about 50 g of barium perchlorate, about 30 g of sodium chloride and 20 ml to 30 ml of 2-propanol in 1 L of water, dissolve and stir well.
- b) **Apparatus** The apparatus consists of an extracted gas oxidizing part, absorption cell (electrolytic cell), coulometric measuring part, etc.
- 1) **Extracted gas oxidizing part** The extracted gas oxidizing part is a part aiming at generating carbon dioxide by oxidizing the extracted carbon monoxide, and consists of tubes connecting a tube filled with iodine pentoxide which is heated at 160 °C to 180 °C in the electric resistance heating furnace and a tube filled with sodium thiosulfate for absorbing iodine which is released when oxidation reaction occurs. An example of the apparatus composition of coulometric method is shown in Figure 6.
 - 2) **Absorption cell (electrolytic cell)** The absorption cell is a cell where the cathode chamber in which catholyte (absorbent) is put in order to absorb the generated carbon dioxide and the anode chamber in which anolyte and barium carbonate are put are combined across the diaphragm (perforated plate), and the platinum electrodes for electrolysis are inserted in both chambers. The size of a platinum electrode should be at least 200 mm². In order to measure the pH of catholyte (absorbent), the reference chamber in which the reference liquid is put is combined across the diaphragm (perforated plate), and a glass electrode is inserted in the cathode chamber and a reference electrode ²⁾ is inserted in the reference chamber. A stirrer is installed so that the carbon dioxide gas introduced from the bottom part of the absorption cell may be sufficiently absorbed (see Figure 6).

If a lot of carbon dioxide flows into an absorption cell at a given time, the absorption of gas will become imperfect. In order to prevent this, an apparatus is provided to stop gas introduction temporarily.

Note ²⁾ Normally, a silver-silver chloride electrode is used.