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JIS K 2609 : 1998

**Crude petroleum and petroleum
products—Determination of nitrogen
content**

ICS 75.080

Descriptors : determination of content, petroleum, petroleum products, nitrogen

Reference number : JIS K 2609 : 1998 (E)

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of International Trade and Industry through deliberations at Japanese Industrial Standards Committee in accordance with the Industrial Standardization Law:

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Crude petroleum and petroleum products— Determination of nitrogen content

1 Scope This Japanese Industrial Standard specifies the method to determine nitrogen content contained in crude petroleum and petroleum products.

- Remarks 1 In this Standard dangerous reagents, procedures, or apparatus may be used, however, this Standard does not necessarily specify every precautions for safe service of them, therefore, prior to their use, it is recommended to decide the prohibitions on safety and hygienic conditions.
- 2 The normative references to this Standard are listed in Attached Table 1.
- 3 The International Standards related to this Standard are listed in Attached Table 2.
- 4 The units and numerical values given in { } in this Standard are based on the traditional units, and appended for informative reference.

2 Classification of testing methods Testing methods are classified into the 3 kinds as shown in Table 1.

Table 1 Classification of testing methods

Kinds of testing methods	Applicable type of oil and limits of nitrogen content (example)		Characteristics (Informative reference)	No. of clause
Macro Kjeldahl method	Lubricating oil	0.03 mass % to 0.10 mass %	This method is well known as a wet analysis method for nitrogen in organic compounds. This is a partly modified Kjeldahl method and is regarded as a basic method in this Standard. Since the amount of a sample to be used for a test is as plentiful as 0.2 g to 2 g, the time for decomposition of sample is long (7 h to 10 h). The method for determination of nitrogen is a neutralization titrimetry.	3
	Heavy oil	0.01 mass % to 2.0 mass %		
Chemiluminescence method	Naphtha Kerosine Gas oil	1 mass ppm or more	This is an instrumental analysis, by which nitrogen content can quickly be determined making use of a working curve prepared previously. Comparing with microcoulometric titration method, it has a merit that the maintenance and management of testing apparatus can easily be done.	4
	Crude oil Lubricating oil Heavy oil	0.01 mass % or more		
Microcoulometric titration method	Naphtha Kerosine Gas oil	2 mass ppm or more	This is an instrumental analysis, by which nitrogen content can quickly be determined, but the recovery rate of nitrogen shall preliminarily be obtained using reference material.	5
	Crude oil Lubricating oil Heavy oil	0.01 mass % or more		

- Remarks 1 In the case where the test result obtained by the microcoulometric titration or chemiluminescence method, in which 0.01 % or more of nitrogen was measured, is doubtful, a macro Kjeldahl method shall be depended.
- 2 The determining method for nitrogen using a micro Kjeldahl method is shown in Informative reference (Testing method for nitrogen using a micro Kjeldahl method).

Informative reference : For inspection of accuracy (bias) of test result, it is preferable to use the nitrogen-content standard sample (reference material) certified by the Japan Petroleum Institute.

Further, for the statistical verification method for accuracy, it is preferable to use **JIS Z 8402**.

3 Macro Kjeldahl method

3.1 Principle of testing method Heat a sample in concentrated sulfuric acid in which catalyst has been put, decompose it, by which nitrogen contained in the sample will be changed into ammonium sulfate, add strong alkaline, and distill it with steam. Make ammonia generate, and let it be absorbed into boric acid solution, and acid-base titrate it with sulfuric acid standard solution, to find the content of nitrogen.

Informative reference 1 When the sample contains additives in which nitrogen compounds with nitrogen-nitrogen bond or nitrogen-oxygen bond have been mixed, this testing method may fail to accurately determine nitrogen content.

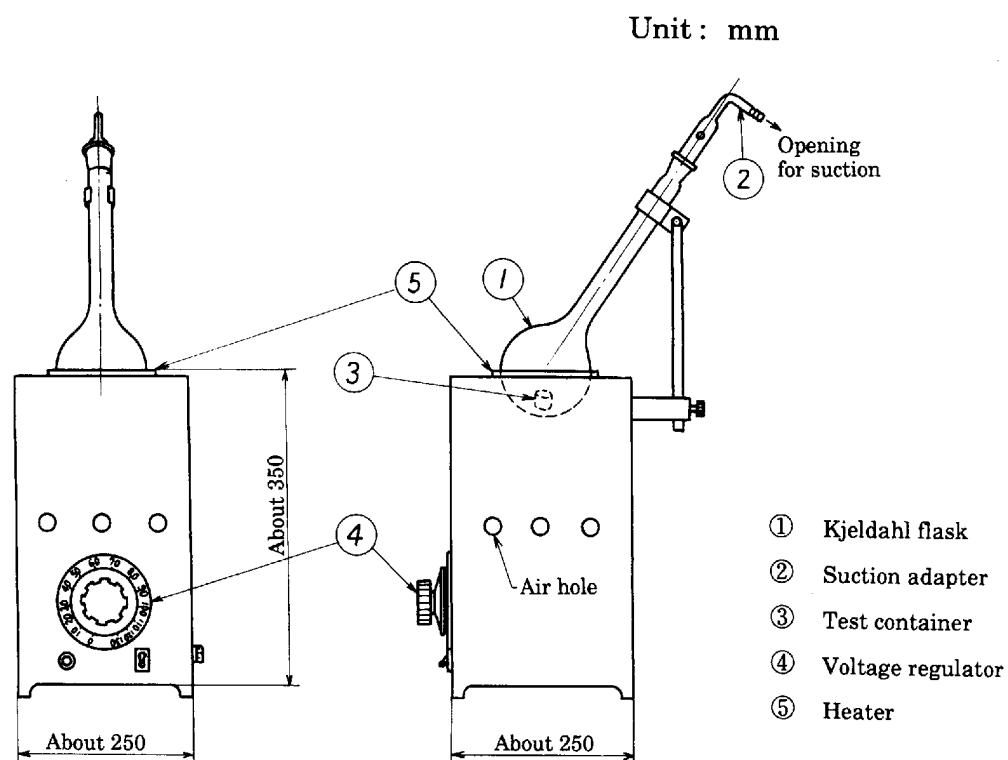
2 This method has been established with reference to **ASTM D 3283-92**.

3.2 Testing apparatus of Macro Kjeldahl method The apparatus is composed of the following from (1) to (6), and its examples are shown in Fig. 1 and Fig. 5.

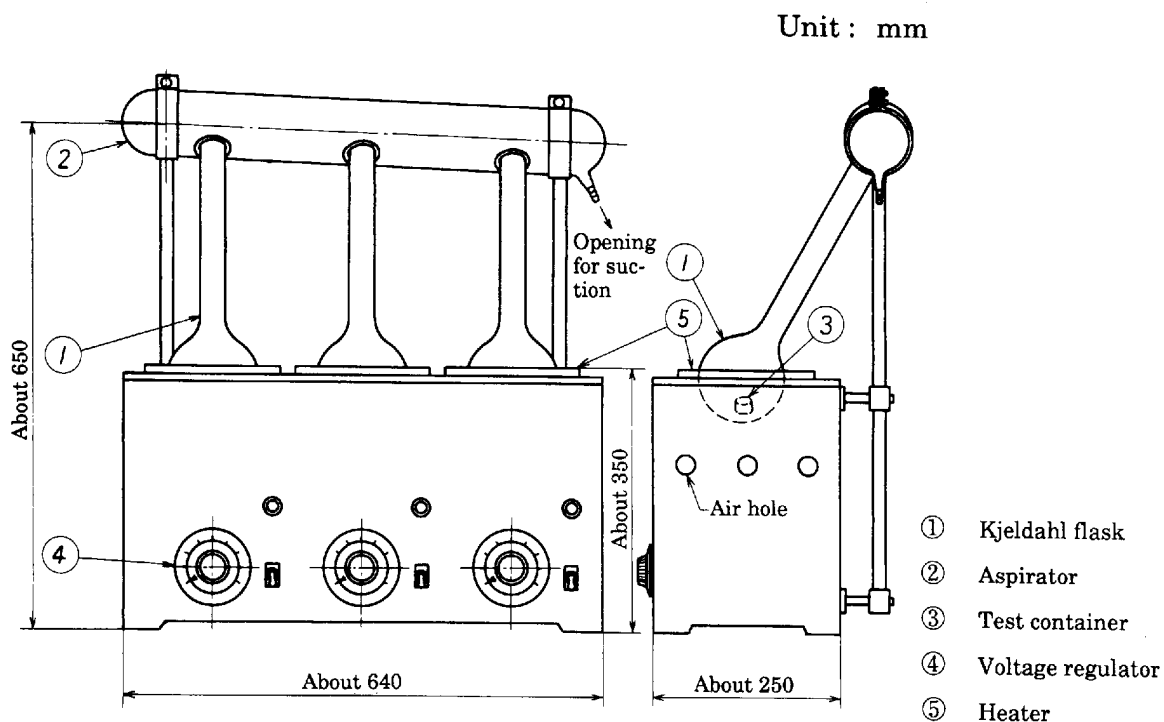
(1) **Sample-decomposing device of Macro Kjeldahl method** Heating device by gas heater or electric heater⁽¹⁾, by which the contents in Kjeldahl flask can be heated and maintained at 360 °C to 380 °C.

Fig. 1 shows an example of electric heating type.

Note (1) It is adequate to use the heater of about 750 W electric capacity (per one unit).



For one unit



For 3 units

**Fig. 1 Sample-decomposing device of Macro Kjeldahl method
(example of electric heating type)**

(2) **Kjeldahl flask** The Kjeldahl flask ground in common, shown in Attached Fig. 14 or Attached Fig. 15 specified in **JIS R 3503**, and with 500 mL or 1 000 mL nominal capacity.

(3) **Test container** Made of glass, with a shape as shown in Fig. 2.

Remarks : The container shown in Fig. 208 specified in **JIS K 2839** is corresponding to this.

Unit : mm

Quality : Borosilicate glass-1

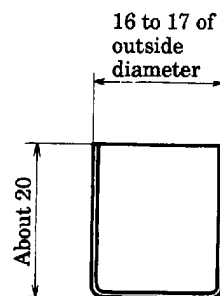


Fig. 2 Test container

Informative reference : Related standard **ASTM D 3228**

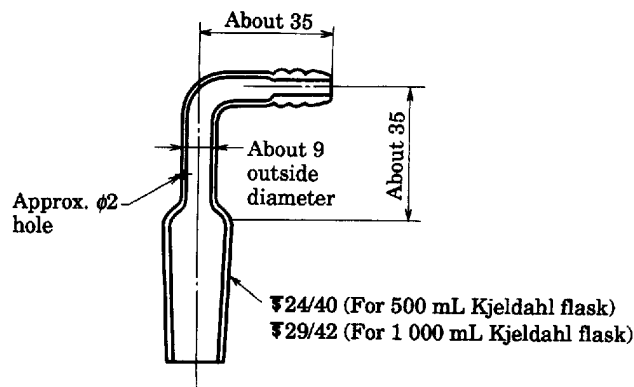
(4) **Suction adapter or aspirator** Suction adapter is made of glass, and shaped as shown in Fig. 3.

Aspirator is made of glass, and shaped as shown in Fig. 4.

Remarks : The adapter is as shown in Fig. 209 specified in **JIS K 2839**. The aspirator corresponds to the one shown in Fig. 210 specified in **JIS K 2839**.

Unit : mm

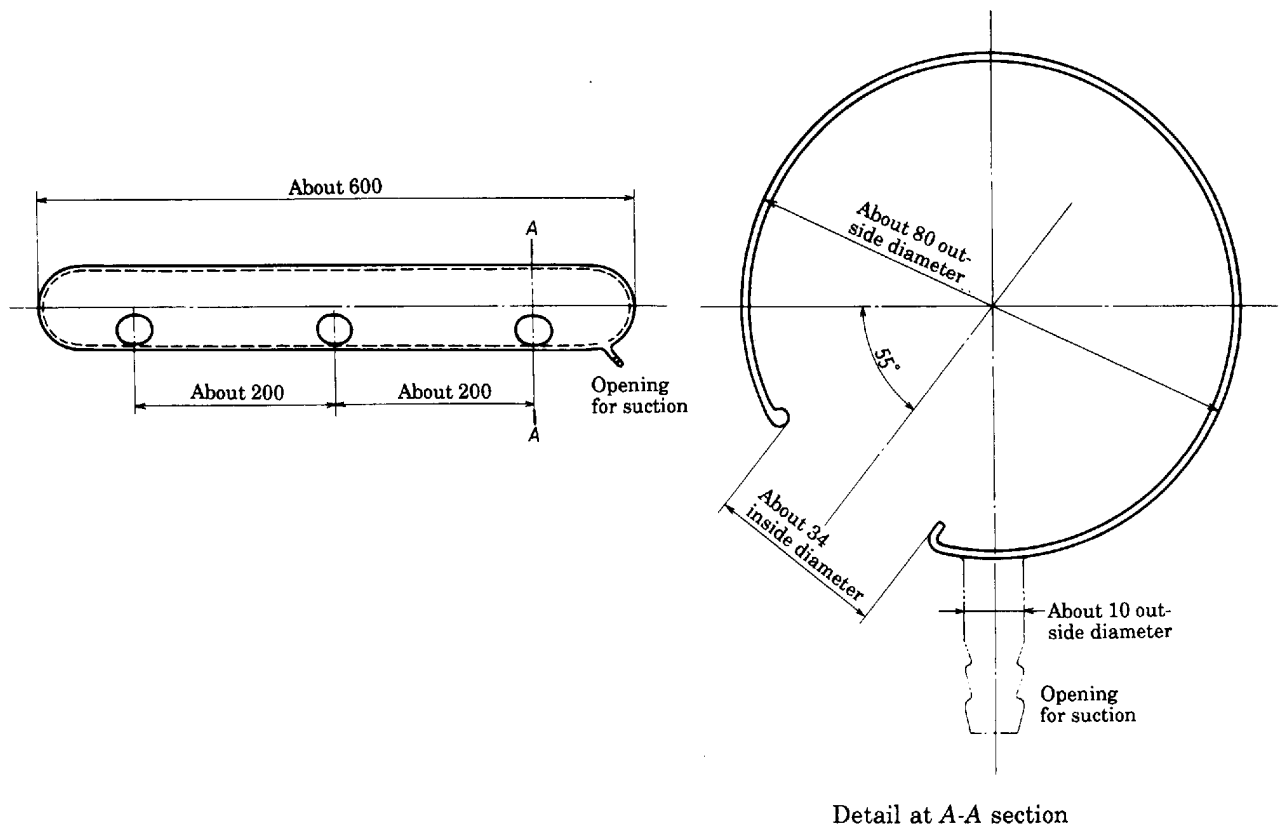
Quality : Borosilicate glass-1



Informative reference : Related standard **ASTM D 3228**

Fig. 3 Suction adapter

Unit : mm

**Fig. 4 Aspirator**

- (5) **Macro Kjeldahl steam distiller** The distiller is composed of the following from (a) to (e), and its example is shown in Fig. 5.

6
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Unit : mm

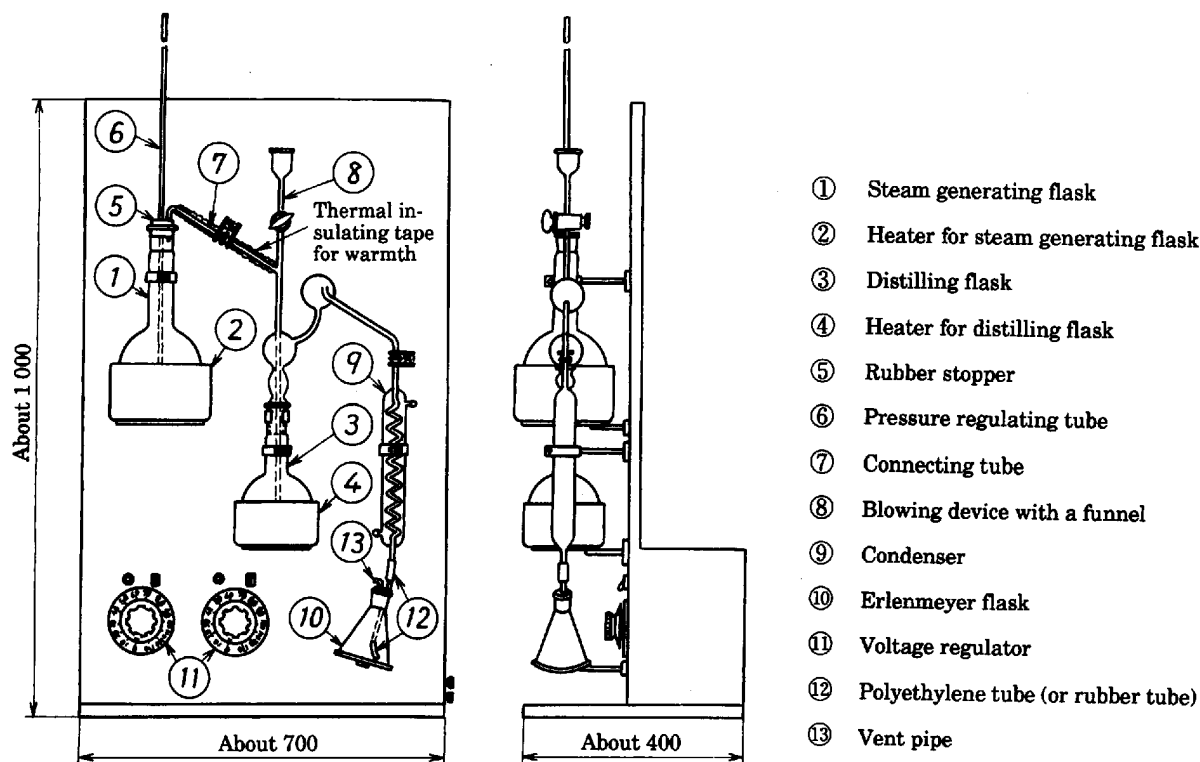


Fig. 5 Macro Kjeldahl steam distiller (example)

- (a) **Steam generating flask** Steam generating flask is a round-bottom flask as shown in Attached Fig. 4 specified in **JIS R 3503**, and with 1 000 mL or 2 000 mL nominal capacity.
- (b) **Distilling flask** Distilling flask is a short neck round-bottom flask ground in common, as shown in Attached Fig. 5 specified in **JIS R 3503**, and with 1 000 mL nominal capacity.
- (c) **Blowing device with a funnel** Made of glass, shaped as shown in Fig. 6.

Remarks : The device shown in Fig. 211 specified in **JIS K 2839** corresponds to this.

Unit : mm

Quality : Borosilicate glass-1

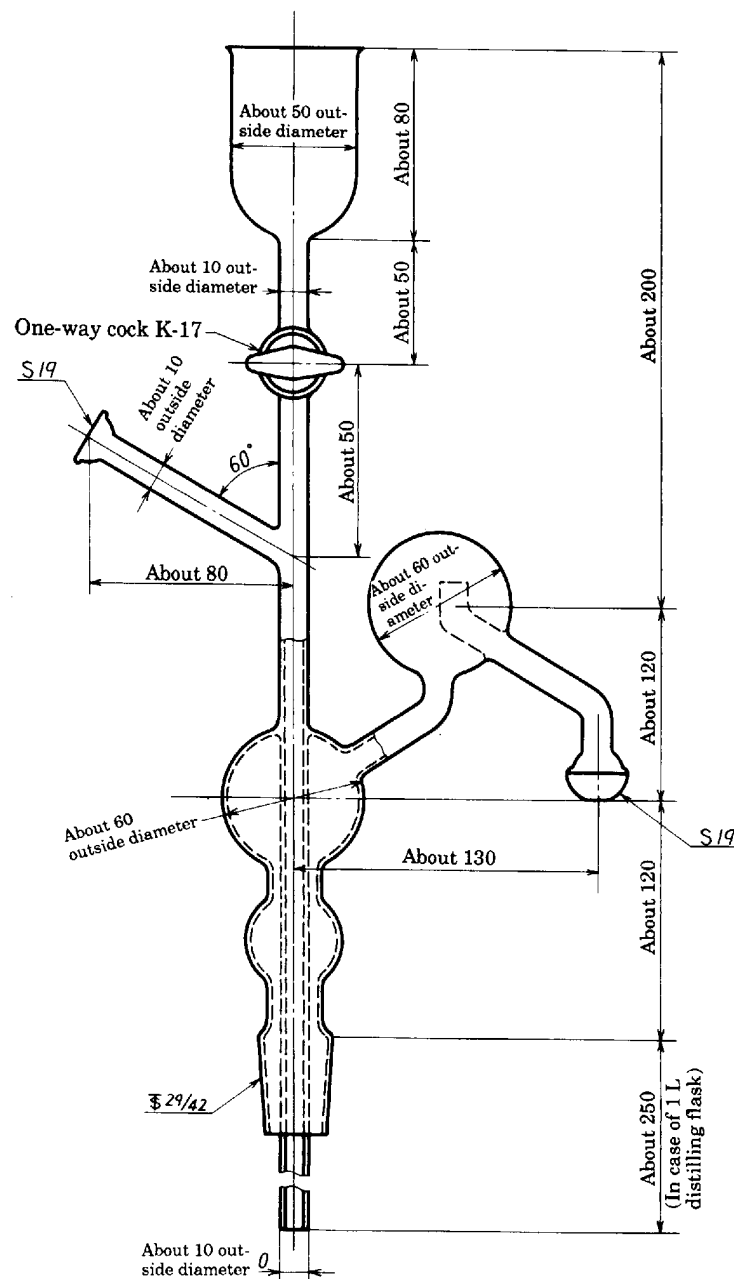


Fig. 6 Blowing device with a funnel

- (d) **Condenser** Made of glass, shaped as in Fig. 7.

Remarks : The condenser shown in Fig. 212 specified in **JIS K 2839** corresponds to this.

- (e) **Connecting tube** Made of glass, shaped as in Fig. 8.

Remarks : The connecting tube shown in Fig. 213 specified in **JIS K 2839** corresponds to this.

8
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Unit : mm
Quality : Borosilicate glass-1

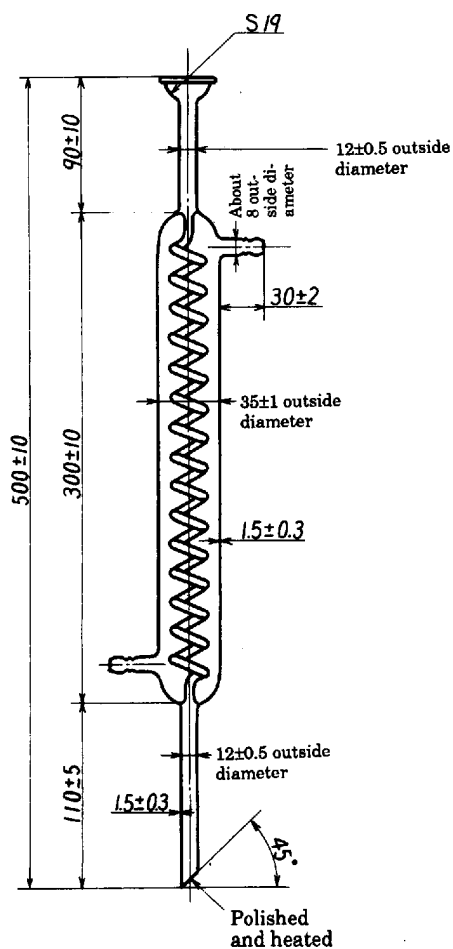


Fig. 7 Condenser

Unit : mm
Quality : Borosilicate glass-1

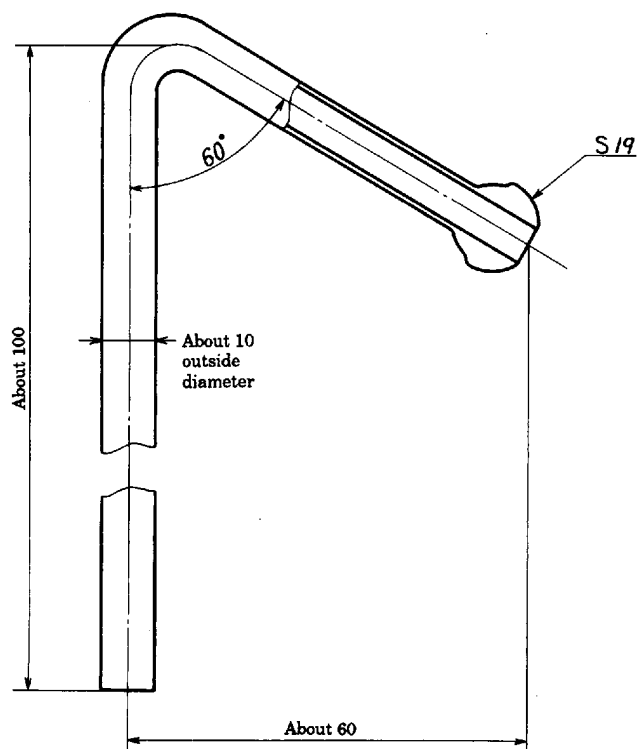


Fig. 8 Connecting tube

(6) **Buret** Made of glass, shaped as in Fig. 9.

Remarks : The connecting tube shown in Fig. 100 specified in **JIS K 2839** corresponds to this.

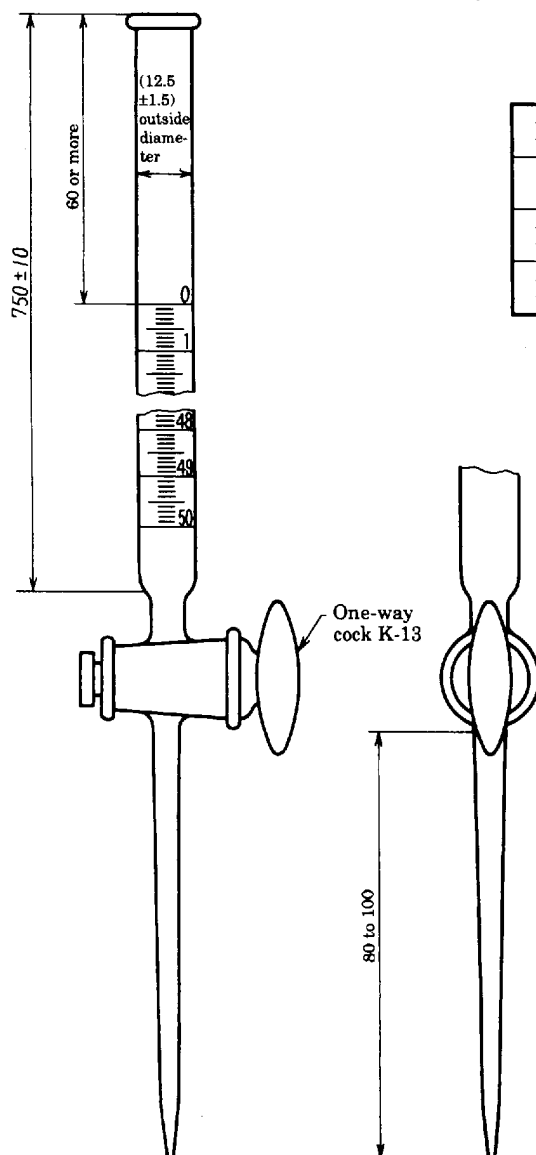
Unit : mm

Quality : Borosilicate glass-2 or more

Scale

Unit : mL

Range	From 0 to 50
Scale quantity	0.1
Long scale line	Every 1
Numbering	Every 1



Informative reference : The buret shown in Fig. 9 is only an example, therefore, other shaped and dimensioned one is permissible when it has the same function as that of the shown.

Fig. 9 Buret

3.3 Reagents The reagents employed in macro Kjeldahl method are as follows.

- (1) **Sulfuric acid** Specified in **JIS K 8951**.
- (2) **Sucrose** Specified in **JIS K 8383**.
- (3) **Water** A3 class water specified in **JIS K 0557**.

- (4) **Sodium hydroxide solution (50 mass %)** Take 500 mL of water in a stainless steel container, dissolve 500 g of sodium hydroxide specified in **JIS K 8576**, and allow it to cool to room temperature⁽²⁾.

Note (2) When the solution is prepared and thereafter treated, protective gloves or protective goggles are necessary.

- (5) **Sodium hydroxide solution (0.04 mass %)** Dissolve 0.4 g of sodium hydroxide specified in **JIS K 8576** in water, and dilute it with water to make total 1 000 mL.
- (6) **Catalyst** Mix copper sulfate specified in **JIS K 8983** and potassium sulfate specified in **JIS K 8962** by the ratio of 1 to 25 (mass ratio).

Remarks : Potassium sulfate shall be prepared as follows; pulverize its adequate amount, transfer into a porcelain dish, put it in an electric furnace, raise gradually its temperature from 100 °C or lower to 500 °C to 600 °C, heat it for 12 h, and allow it to cool in a desiccator.

- (7) **Boiling stone** Heat tips of carborundum or small pieces of porcelain in sulfuric acid in boiling for 30 min, eliminate nitrogen compounds, wash them with water, and dry up.
- (8) **Boric acid solution (0.4 mass %)** Dissolve 4.0 g of boric acid specified in **JIS K 8863** in 1 000 mL water.
- (9) **Bromophenol blue indicator** Dissolve 0.10 g of bromophenol blue specified in **JIS K 8844** in 50 mL of ethanol specified in **JIS K 8102**, and then add water to make total 100 mL.
- (10) **0.05 mol/L sulfuric acid standard solution** Dissolve 3 mL of sulfuric acid in 1 L of water. The molar concentration of this solution shall be obtained as follows.
- (a) Put 5 g or less of sodium carbonate (anhydrous) specified in **JIS K 8005** into a platinum crucible, heat it at 600 °C for about 1 h, and allow it to cool in a desiccator keeping magnesium perchlorate as a desiccant for 0.5 h to 1 h.
- (b) Weigh 0.13 g to 0.16 g of sodium carbonate (anhydrous) prepared at (a) to the nearest 0.1 mg, dissolve it in 20 mL of water, and titrate the solution with 0.05 mol/L sulfuric acid standard solution after adding bromophenol blue indicator. When it reached near an end point, boil it to expel carbon dioxide, and after cooling it, continue the titration. Make it an end point when bluish violet of indicator turns to yellow.
- (c) Calculate molar concentration of 0.05 mol/L sulfuric acid standard solution according to the following formula, and round off the result to four decimals according to the rule in **JIS Z 8401**.

$$C = \frac{M}{0.1060V} \times \frac{P}{100}$$

where, C : molar concentration of 0.05 mol/L sulfuric acid standard solution (mol/L)

M : mass of sodium carbonate (anhydrous) weighed at (b) (g)

V : volume of 0.05 mol/L sulfuric acid standard solution needed for titration (mL)

P : content of sodium carbonate (mass %)

- (11) **0.005 mol/L sulfuric acid standard solution** Dilute accurately ten times 0.05 mol/L sulfuric acid standard solution with water using a pipet and volumetric flask. The molar concentration of this sulfuric acid standard solution is one-tenth of that of stock solution.
- (12) **Mixed indicator**⁽³⁾ Mix the following 2 kinds of solution by equal volume. This mixed solution is stored in a brown colored bottle, but it cannot be used when one week or more elapsed after it was prepared.
- (a) Dissolve 0.125 g of methyl red specified in **JIS K 8896** in 100 mL of ethanol specified in **JIS K 8102**.
- (b) Dissolve 0.083 g of methylene blue specified in **JIS K 8897** in 100 mL of ethanol specified in **JIS K 8102**.
- Note (3) Instead of this mixed solution, 0.1 % solution of methyl purple is available.
- (13) **Zinc** Specified in **JIS K 8012**.

3.4 Sampling and preparation of sample Carry out taking of the primary sample and the preparation of the secondary sample as shown in **JIS K 2251**, or take and prepare the sample with the method conforming to these methods.

3.5 Procedures for test The procedures for macro Kjeldahl method shall be as follows.

(1) **Decomposition**

- (a) Weigh the quantity of sample as shown in Table 2 in a test container to the nearest 1 mg, and put it into a Kjeldahl flask, whose mass has been weighed, together with the test container. Then add sulfuric acid depending on its quantity, place 3 to 5 tips of boiling stones whose mass has been known into it, and then shake them.

Table 2 Weighed mass of sample and quantity of sulfuric acid

Nitrogen content mass %	Weighed mass g	Quantity of sulfuric acid mL
0.05 or less	2	50
Over 0.05 up to and incl. 0.1	1	40
Over 0.1 up to and incl. 0.25	0.5	30
More than 0.25	0.2	30

- (b) Place the Kjeldahl flask on macro Kjeldahl decomposing device for sample, attach either a suction adapter or aspirator, and heat it while making suction.

Remarks : When an aspirator is used, in order to make effective suction, stuff glass wool in the gap between the neck of Kjeldahl flask and connecting part of the aspirator.

- (c) Heat gradually it to get high temperature carefully lest the contents of the Kjeldahl flask should violently bubble. When it shows violent bubbling, weaken heating. If weakening is not effective for violent bubbling, supplement 10 mL to 15 mL of sulfuric acid.
- (d) After the bubbling was depressed, adjust heating so as to allow the vapor of sulfuric acid to condense and to reflux at the position about $\frac{1}{2}$ to $\frac{3}{4}$ of the neck of the Kjeldahl flask, wash completely down the carbon compounds stuck to the neck of the Kjeldahl flask with refluxed sulfuric acid, and heat on as it is until the contents become brown nonviscous liquid.
- (e) Stop heating, allow the Kjeldahl flask to stand for about 10 min, and add 25 g of catalyst. Again, heat it to allow the sulfuric-acid vapor to reflux at the neck of the Kjeldahl flask, and when the contents become colorless or dark green transparent liquid, heat it on for another 30 min to 60 min to decompose the sample.
- (f) After decomposition has finished, allow it to cool to room temperature, and weigh the mass of the Kjeldahl flask together with its contents.

Making use of the following formula, calculate the final catalyst ratio, and confirm it falls in the range from 1.0 to 1.5. When it is smaller than 1.0, heat it again, and evaporate sulfuric acid. When larger than 1.5, retry the procedures from (a). In this case, add sulfuric acid 5 mL more than the quantity shown in Table 2.

$$R = \frac{1.8C}{S}$$

$$= \frac{1.8C}{A - (C + F + B + V)}$$

where, R : final catalyst ratio

C : added quantity of catalyst (= 25) (g)

S : remained sulfuric acid (g)

A : mass of the Kjeldahl flask containing the contents after decomposition was completed (g)

F : mass of empty Kjeldahl flask (g)

B : mass of boiling stone (g)

V : mass of test container (g)

- (g) Then, add gradually 300 mL of water into the Kjeldahl flask while the flask is being cooled with an icy bath, and dissolve the isolated salt.

(2) Steam distillation

- (a) Transfer liquid only kept in the Kjeldahl flask into a distilling flask, rinse inside of the Kjeldahl flask with 100 mL water, and add washing into the flask. Add 1 g of zinc in it.
- (b) Take 50 mL of boric acid solution (0.4 mass %) into a 500 mL Erlenmeyer flask, and assemble macro Kjeldahl steam distiller so as to let the end point of polyethylene tube (or rubber tube) dip in the solution by tilting the 500 mL Erlenmeyer flask (See Fig. 5). While flowing cooled water through a condenser, add little by little sodium hydroxide solution (50 mass %) from the funnel into the distilling flask by double quantity, which is expressed with mL unit, of remained sulfuric acid (g)⁽⁴⁾.

Note (4) This procedure would be easy if it is carried out while the air in the system is being absorbed through vent pipe attached on the stopper of the 500 mL Erlenmeyer flask.

- (c) Carry out steam distillation with care not to make bumping in both steam-generating flask and the solution in distilling flask by moderately heating. When the solution kept in the 500 mL Erlenmeyer flask becomes 120 mL to 150 mL⁽⁵⁾, disconnect the stopper, lift up the end point of the polyethylene tube (or rubber tube) in the 500 mL Erlenmeyer flask from the solution level, and wash it with a little water. Then, continue steam distillation for about 1 min while keeping the end point of the polyethylene tube (or rubber tube) in the 500 mL Erlenmeyer flask off from solution level, and stop heating. Wash the end point of the polyethylene tube (or rubber tube) with a little water.

Note (5) When the quantity of solution in the 500 mL Erlenmeyer flask becomes near 150 mL, the salt in the distilling flask deposits, which carries easily bumping in the solution, therefore adjust heating so as not to make the splashes enter in distillate.

- (3) **Titration** Add 0.5 mL of mixed indicator into the solution kept in the 500 mL Erlenmeyer flask, titrate it with 0.005 mol/L sulfuric acid standard solution, and make it an end point when pale green turns reddish violet⁽⁶⁾⁽⁷⁾.

Notes (6) When the end point is hardly judged, carry out as follows.

Prepare another 500 mL Erlenmeyer flask, put 50 mL boric acid solution (0.4 mass %), add water to let its volume the same as that of titration solution, then, add 0.5 mL of mixed indicator and a couple of drops of sodium hydroxide solution (0.04 mass %) to make its color green. Acid-base titrate this solution with 0.005 mol/L sulfuric acid standard solution to color this solution. And compare this color with the color obtained by the acid-base titration obtained from test solution.

- (7) In case of using methyl purple of indicator, the end point is given when greyish blue turns purple.

- (4) **Blank test** Instead of sample, take sucrose, and carry out the procedures from (1) to (3)⁽⁸⁾.

Note (8) The amount of sucrose to be used shall be chosen on Table 3 depending on the quantity of sulfuric acid used for decomposition.

The quantity of catalyst shall be 25 g in any case.