

JIS

JAPANESE INDUSTRIAL STANDARD

Crude oil and petroleum products —Determination of sulfur content

JIS K 2541—1996

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JAPANESE INDUSTRIAL STANDARD

J I S

Crude oil and petroleum products—
Determination of sulfur content

K 2541-1996

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

Remarks 1. These testing methods often adopt dangerous chemicals, procedures, and apparatus, but these methods don't necessarily prescribe all safety measures against them, so, prior to employing them, it is necessary to arrange the forbidden items for keeping suitably safety and health.

2. The standards cited in this Standard are listed in Attached Table 1.

3. The International Standards corresponding to this Standard are listed in Table 1.

Table 1. Corresponding International Standards

Testing method	Corresponding International Standards
Oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method	ISO 4260: 1992 (Petroleum products and hydrocarbons—Determination of sulfur content—Wickbold combustion method)
Radiation-type excitation method	ISO 8754: 1992 (Petroleum products—Determination of sulfur content—Energy-dispersive X-ray fluorescence method)

4. The units and numerical values given in { } in this Standard are based on the traditional units, and are appended for informative reference.

Informative reference: ISO standard designates the radiation-type excitation method as an energy-dispersive X-ray fluorescence method.

2. Classification of testing methods The testing methods shall be classified as shown in Table 2.

Table 2. Classification of testing methods

Classification of testing methods	Example of applicable oils	Measurable range	Applicable clause number
Oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method	Gasoline for automobile, kerosine, gas oil	1 to 300 mass ppm	3.
Microcoulometric titration-type oxidation method		1 to 1000 mass ppm	4.
Combustion tube-type air method	Crude oil, gas oil, heavy oil	0.01 mass % or over	5.
Radiation-type excitation method		0.010 mass % or over	6.
Combustion tube-type oxygen method		0.01 mass % or over	7.
Bomb-type mass method	Crude oil, heavy oil, lubricating oil	0.10 mass % or over	8.
Lamp-type volumetric method	Gasoline for automobile, kerosine	0.002 mass % or over	Informative reference 1
Wavelength-dispersive X-ray fluorescence method	Gasoline for automobile, kerosine, gas oil, heavy oil, crude oil, lubricating oil	0.0010 to 2.50 mass %	Informative reference 2

Remarks 1. When the test result, on crude oil, gas oil and heavy oil, measured by such as radiation-type excitation method, combustion tube-type oxygen method, or bomb-type mass method gives some doubtful condition, follow the results made by combustion tube-type air method.

2. When the test result, on gasoline, kerosine and gas oil, measured by such as oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method or radiation-type excitation method gives some doubtful condition, follow the results made by microcoulometric titration-type oxidation method.

Informative reference (1) The testing method of sulfur content by lamp-type volumetric method is shown in Informative reference 1 (Petroleum products — Determination of sulfur content — Lamp-type volumetric method).

(2) The testing method of sulfur content by radiation-type wavelength-dispersive X-ray fluorescence method, which has been established with making reference to ISO/CD 14596: 1994, is shown in Informative reference 2 (Crude oil and petroleum products — Determination of sulfur content — Wavelength-dispersive X-ray fluorescence method).

3. Oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method

3.1 Principle of test Burn sample in oxyhydrogen flame, produce sulfur oxide, and make the sulfur oxide be absorbed in hydrogen-peroxide solution (3%), to prepare sulfuric acid. For the purpose of determination of sulfur in the absorbing liquid, concentrate the liquid, add buffer solution and acetone into it, and titrate the sulfate ion in the liquid with barium perchlorate standard solution using dimethyl sulfonazo III as indicator, to find the content of sulfur.

Remarks 1. This testing method is suitable for crude oil and petroleum products containing from 1 mass ppm to 10000 mass ppm of sulfur, but especially suitable for the distilled oil containing 300 mass ppm or less.

In case of the sample containing more than 300 mass ppm of sulfur content, measure it by any one of the following.

- (1) Dilute the sample with a suitable sulfur-free solvent, and then burn its whole amount.
 - (2) Instead of burning whole amount of sample, burn its necessary amount.
 - (3) Take an aliquot of the absorbing liquid, and make titration.
2. This testing method cannot be applied to the samples containing 100 mass ppm or over of halogen, 5 mass ppm or over of calcium, 2 mass ppm or over of phosphorus and 2 mass ppm or over of lead, or containing other metals producing insoluble sulfate.

3.2 Reagents The reagents for oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method shall be as follows.

- (1) Oxygen Specified in JIS K 1101.
- (2) Hydrogen Specified in JIS K 0512.
- (3) Acetone Specified in JIS K 8034.
- (4) Solvent Isooctane specified in JIS K 2280, or petroleum solvent containing less than 1 mass ppm of sulfur content.
- (5) Hydrogen peroxide solution (3%) Dilute 1 volume of hydrogen peroxide solution (30%) specified in JIS K 8230 with 9 volume of water. Store this solution in a brown colored bottle.
- (6) Potassium hydrogen phthalate buffer solution (2%) Dissolve 20 g of potassium hydrogen phthalate specified in JIS K 8809 in water to make total 1000 ml.
- (7) Dimethyl sulfonazo III indicator Dissolve 0.1 g of dimethyl sulfonazo III [2,7-bis(sulfo-4-methylphenyl)azo-1,8-dihydroxynaphthalene-3,6-disulfonic acid sodium salt] which is the best quality one on the market, in 100 ml of water ⁽¹⁾. Store this indicator in a brown colored bottle.

Note ⁽¹⁾ If the color change at end point becomes obscure, reprepare it.

- (8) Barium perchlorate standard solution (0.0025 mol/l) Weigh about 0.98 g of barium perchlorate (trihydrate salt) specified in JIS K 9551, add small quantity of water and 4 or 5 drops of perchloric acid solution (10 vol %) which has been prepared from perchloric acid specified in JIS K 8223, transfer it into a 1000 ml measuring flask, and add water up to the marked line.

The standardization of this solution shall be carried out as follows.

- (a) Weigh accurately about 0.44 g of potassium sulfate specified in JIS K 8962, which has been dried at 105°C to 110°C for 3 h or longer, to the nearest 1 mg, transfer it into a 1000 ml measuring flask, and add water up to the marked line, to prepare potassium sulfate solution.

Calculate concentration of potassium sulfate solution according to the following formula, and round it off to 3 significant figures according to JIS Z 8401.

$$C = \frac{K}{174.27}$$

where, C : concentration of potassium sulfate (mol/l)

K : weighed mass of potassium sulfate (g)

- (b) Take accurately 10 ml of potassium sulfate solution with a transfer pipet into a 200 ml beaker, and add 10 ml of water.
- (c) Add about 50 ml of acetone and 5 ml of potassium hydrogen phthalate buffer solution (2%), drip 4 or 5 drops of dimethyl sulfonazo III indicator, and while stirring it with a magnetic stirrer titrate it with barium perchlorate solution. Make it an end point when solution turns greenish blue from purple and lasts for 1 min or more ⁽²⁾.

Note ⁽²⁾ It's easy to detect an end point when titration is carried out with background of white board.

- (d) Take 20 ml of water, titrate it by the same procedure as in (c), and make it the blank test.
- (e) Calculate the concentration (mol/l) of barium perchlorate standard solution according to the following formula, and round it off to 3 significant figures according to JIS Z 8401.

$$M = \frac{10C}{A - B}$$

where, M : concentration of barium perchlorate standard solution (mol/l)

A : quantity of barium perchlorate solution needed for titration (ml)

B : quantity of barium perchlorate solution needed for blank test (ml)

C : concentration of potassium sulfate solution (mol/l)

- (9) Barium perchlorate standard solution (0.005 mol/l) Weigh about 1.95 g of barium perchlorate (trihydrate salt), and prepare and standardize it by the same procedures as in (8).
- (10) Sulfur reference solution (250 mass ppm) Weigh 0.98 g of di-*n*-butyl sulfide, containing 21.70 mass % to 21.95 mass % of sulfur, into a 100 ml measuring flask whose mass has been known, to the nearest 0.1 mg, add toluene specified in JIS K 8680 for dissolving it, further add toluene up to the marked line, and measure its mass. Then, take its 25 ml into a 250 ml measuring flask with a transfer pipet, and dilute it with toluene up to the marked line.

Calculate the sulfur reference value according to the following formula, and round it off to one decimal place according to JIS Z 8401.

$$A = \frac{0.2187M}{T} \times 10^5$$

where, A : sulfur reference value (mass ppm)

M : weighed mass of di-*n*-butyl sulfide (g)

T : mass of di-*n*-butyl sulfide and toluene weighed in a 100 ml measuring flask (g)

Remarks: Instead, dihexyl disulfide (containing 27.36 mass % sulfur) or dibenzothiophene (containing 14.7 mass % sulfur) may be used as the reagent of sulfur reference solution.

- (11) Sulfur reference solution (50 mass ppm) Take 20 ml of sulfur reference solution (250 mass ppm) into a 100 ml measuring flask using a transfer pipet, and add toluene specified in JIS K 8680 up to the marked line. This sulfur reference solution shows the value of $A/5$, and is rounded off to one decimal place.
- (12) Sulfur reference solution (5 mass ppm) Take 2 ml of sulfur reference solution (250 mass ppm) into a 100 ml measuring flask using a transfer pipet, and add toluene specified in JIS K 8680 up to the marked line. This sulfur reference solution shows the value of $A/50$, and is rounded off to one decimal place.
- (13) Water Follow A3 of JIS K 0557.

3.3 Oxyhydrogen flame combustion-type tester The tester is composed of (1) to (3), and Fig. 1 and Fig. 2 show an example of its construction.

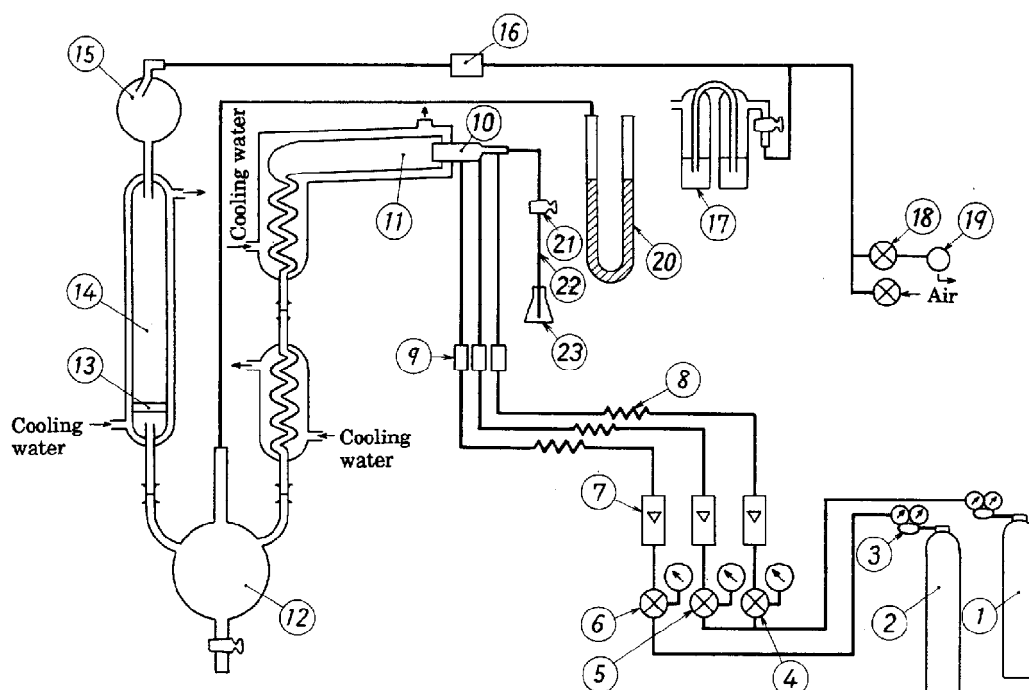
- (1) Oxyhydrogen flame burning apparatus This is composed of a burner and combustion tube as shown in Fig. 1.

To keep the safety during procedures, the following accessory devices shall be attached.

- (a) Discharge valve Capable of automatically discharging the combustion gas in the atmosphere when a power failure takes place.

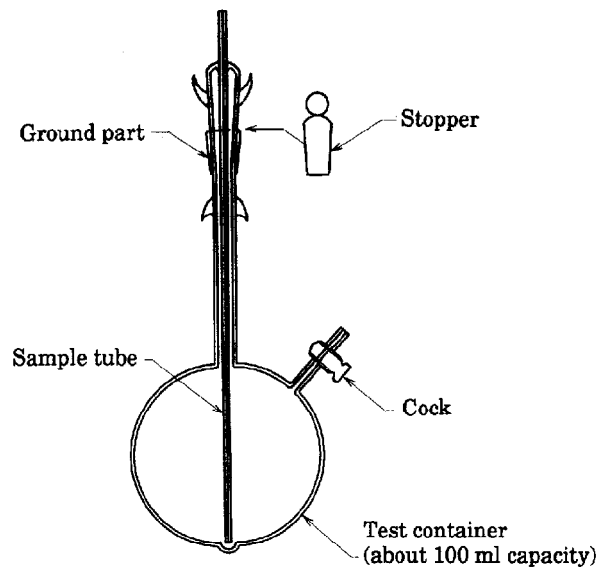
- (b) Preventing device of back fire Capable of preventing going back of burner flame into oxygen and hydrogen line.
- (c) Protecting board Attach this in front of the apparatus.
- (2) Vacuum pump Oil-less vacuum pump with at least 25 l per min of evacuating capacity.
- (3) Test container A glass container suitably sized for the taken quantity of sample. In case of volatile sample at ordinary temperature, it shall be hermetically closable, as shown in Fig. 2, for preventing volatile loss.

Fig. 1. Construction of tester for oxyhydrogen flame combustion-type dimethyl sulfonazo III titration (example)



- | | |
|---|-----------------------------------|
| ① Compressed oxygen | ⑬ Filter |
| ② Compressed hydrogen | ⑭ Absorption tube |
| ③ Pressure regulator | ⑮ Trap of absorption tube |
| ④ Primary pressure reducing valve of oxygen | ⑯ Discharge valve |
| ⑤ Secondary pressure reducing valve of oxygen | ⑰ Indicator of pressure balance |
| ⑥ Pressure reducing valve of hydrogen | ⑱ Pressure-reducing control valve |
| ⑦ Flowmeter | ⑲ Vacuum pump |
| ⑧ Resistance tube | ⑳ Manometer |
| ⑨ Back-fire preventing device | ㉑ Cock for sample |
| ⑩ Burner | ㉒ Tube for sample |
| ⑪ Combustion tube (made of quartz) | ㉓ Test container |
| ⑫ Drain trap | |

Fig. 2. Hermetically closing-type test container (example)



3.4 Sampling method Carry out sampling according to the primary sampling method and the secondary sample preparation method specified in JIS K 2251 or similar method.

3.5 Procedures of test The testing procedures for oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method shall be as follows.

- Remarks**
1. Tester has a lot of glass devices and there is a high temperature burning of oxyhydrogen flame, therefore it is crucial to always keep correct procedures for safety.
 2. Just in case of such unusualnesses as the cut off of water supply, power failure, and stop of vacuum pump while burning, establish beforehand the countermeasures and its concrete operations such as interruption of burning fuel, drawing out of burner, shut off of hydrogen pressure-reducing valve, and so on.

Informative reference: Combustion conditions of fuel such as flow rate and pressure of oxygen and hydrogen, and pressure inside the system, differ somewhat according to the type of apparatus, therefore it would be better to follow the instruction manual issued by the manufacturer. The combustion conditions of fuel are exemplified in the following Informative reference Table 1.

Informative reference Table 1. Combustion conditions
of fuel (example)

Item	Combustion conditions of fuel
Pressure of hydrogen	290 kPa (3 kgf/cm ²)
Pressure of oxygen	400 kPa (5 kgf/cm ²)
Flow rate of primary oxygen	6.5 to 8.5 l/min
Flow rate of secondary oxygen	3.5 to 5.0 l/min
Pressure-reducing degree in system	$0.13 \times 10^5 - (26.66 \text{ to } 39.99) \times 10^2 \text{ kPa}$ [atmospheric pressure - (20 to 30 mmHg)]
Flow rate of hydrogen	4.0 to 5.0 l/min

(1) Preparation of tester

- (a) Confirm that there is no leakage at the connection of gas pipe and that glass parts have been inside cleaned.
- (b) Confirm that the quantity of oxygen and hydrogen in bombs is enough for combustion procedure, and control the pressure of gas entering inside the tester to become specified value (Informative reference Table 1) using a pressure regulator.
- (c) Put on such protecting wear as a face protector, protecting goggles, leather gloves, and so on.
- (d) Run a vacuum pump, insert a burner in a combustion tube, open the primary and secondary pressure reducing valves of oxygen while keeping the burner with hands, and control to get the specified flow rate (Informative reference Table 1) with observing the flowmeter. Then, open pressure-reducing control valve, and control inside the system to get specified pressure (Informative reference Table 1).
- (e) Circulate cooling water inside a cooling system.
- (f) Disconnect the trap of absorption tube, place 50 ml of hydrogen peroxide solution (3%) inside the absorption tube, and again connect the trap at its original position.
- (g) Disconnect the burner, and hold it in the burner holder.

(2) Weighing of sample Weigh the sample, taken as shown in 3.4, into a test container by the amount given in Table 3, to the nearest 10 mg.

Remarks 1. Sample containing more than 300 mass ppm of sulfur Weigh sample with reference to Table 3 so as to meet the approximate value of contained sulfur in sample, and add sulfur-free solvent to mix them well. This diluted sample shall be burned as a whole.

2. Sample with consistency or abundant in aromatic compounds
After weighing the quantity shown in Table 3, add sulfur-free solvent to mix them well. This diluted sample shall be burned as a whole.

Table 3. Weighing of sample

Approximate value of sulfur (mass ppm)	Amount of sample to be weighed (g)
1 or over to and excl. 10	50 to 30
10 or over to and excl. 30	30 to 20
30 or over up to and incl. 300	20 to 5

(3) Combustion

- (a) Open the pressure reducing valve of hydrogen, control to get the specified flow rate (Informative reference Table 1) with observing a flowmeter, and expel the air staying inside by passing hydrogen for 30 s or longer.
- (b) While holding the burner in the burner holder, ignite the gas by bringing an igniter ⁽³⁾ near the tip of the burner. In this time, be careful the flame of a burner, and confirm there happens no back fire ⁽⁴⁾.

Then, with care not to make the burner flame heat the ground place of a combustion tube, insert quickly the burner into the combustion tube.

Notes ⁽³⁾ Use such as a gas lighter.

Never use a match.

- ⁽⁴⁾ Back fire can be recognized by observing, but it also makes the ground part of a burner hot, which can be felt by hand. If back fire takes place, raise a little the pressure of hydrogen.
- (c) Confirming the specified pressure is kept inside the system, put the sample tube until it reaches bottom of the sample container, open gradually the cock for sample, and burn the sample. In this time, control the flame length of the burner by a sample cock or a pressure-reducing control valve, and then incomplete burning ⁽⁵⁾ can be prevented.

Boiling of water for cooling a combustion tube may result in danger to destroy the combustion tube by its vibration, in this case, take such countermeasures as increasing the quantity of cooling water or making the rate of burning slow.

Note ⁽⁵⁾ When carbonizing is found in a combustion tube due to incomplete combustion, stop quickly burning procedure, and clean inside the tube. If ordinary cleaning cannot remove the carbonized matter, wash it with warm nitric acid, and then wash with water enough. If carbonizing is found in a burner, place vertically the burner in an electric furnace, and remove it by heating at about 700°C while passing air flow.

- (d) Burn the sample just before the sample tube inhales air, close a cock of sample, and take out the test container. Wash inside the removed test container with solvent, place again the sample tube until it reaches bottom of the sample container, open gradually the cock for sample, and burn the washing liquid. Repeat two or three times this washing and burning procedures.

Remarks: Sample containing more than 300 mass ppm of sulfur
When the combustion of whole quantity of sample is not needed, burn the required quantity, close the sample cock, take out the sample container, then in order to burn the sample remained in a sample tube, exchange the sample container, and burn it using only solvent.

The test container, which has been disconnected, shall be quickly weighed, and the mass of the sample which has been burnt be measured.

(4) Stop

- (a) When the combustion of sample ends, close the sample cock, control to get specified pressure inside the system, draw out the burner while oxyhydrogen gas is burning, and hold it in a burner holder.
- (b) Immediately shut orderly the pressure reducing valves of hydrogen, primary oxygen, and secondary oxygen, then further shut the main valves of oxygen and hydrogen bombs.
- (c) After allowing the pressure inside the system to be atmospheric pressure by closing a pressure-reducing control valve, and stop the vacuum pump.

Remarks: Sample containing more than 300 mass ppm of sulfur In case of titration of aliquot taken from absorbing liquid, pass air for 2 or 3 min before closing a pressure-reducing valve in order to expel carbon dioxide which has dissolved in the absorbing liquid.

(5) Determination of sulfate ion in absorbing liquid

- (a) Wash the trap of absorption tube, combustion tube and absorption tube with water, and collect them into a drain trap together with absorbing liquid.
- (b) Transfer the solution of the drain trap into a 500 ml beaker, wash the trap with water, transfer the washings into the 500 ml beaker, heat it to concentrate up to 20 ml to 50 ml, and allow it to cool to room temperature.
- (c) Add 5 ml of potassium hydrogen phthalate buffer solution (2%) into the 500 ml beaker, add acetone about double volume of whole solution in the beaker, and drip 4 or 5 drops of dimethyl sulfonylazo III indicator.
- (d) Choose barium perchlorate standard solution in Table 4 depending upon sulfur content in the sample, and titrate (2) the solution while stirring with a magnetic stirrer. Make it an end point when the solution turns greenish blue from purple and lasts for at least 1 min.

Table 4. Barium perchlorate standard solution for titration

Sulfur content in sample (mass ppm)	Concentration of barium perchlorate standard solution (mol/l)
1 or over to and excl. 30	0.0025
30 or over up to and incl. 300	0.005

Remarks: Sample containing more than 300 mass ppm of sulfur In case of titration of aliquot taken from absorbing liquid, transfer both the solution in a drain trap and washings of the drain trap into a 300 ml measuring flask, add water up to the marked line, mix them well, take 20 ml to 50 ml aliquot into a 500 ml beaker with a transfer pipet, and then titrate it as shown in (c) and thereafter.

- (6) Blank test Blank test shall be carried out as follows: take only oxygen and hydrogen, burn them in the same procedures and duration as those for the sample, and titrate it as shown in (5).

Remarks: Sample containing more than 300 mass ppm of sulfur When an aliquot was taken from absorbing liquid after test burning and was titrated, take similarly an aliquot from the absorbing liquid for the blank test, and titrate it.

3.6 Calculation method and result Calculate the sulfur content by oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method according to the following formula, and round it off to whole number according to JIS Z 8401.

$$S = \frac{32.06M(A - B)}{W} \times 1000$$

where, S : sulfur content (mass ppm)

M : concentration of barium perchlorate standard solution (mol/l)

A : quantity of barium perchlorate standard solution needed for titration of absorbing liquid for sample (ml)

B : quantity of barium perchlorate standard solution needed for titration of absorbing liquid for blank test (ml)

W : weighed mass of sample (g)

Remarks: Sample containing more than 300 mass ppm of sulfur In case of taking aliquot and titrating at 3.5 (5), multiply $(A - B)$ by [(whole quantity of absorbing liquid) (ml)/(quantity of aliquot) (ml)].

When the whole quantity of sample is not burnt for direct measurement, the “ W ” in the formula shall be replaced by the quantity of sample which has been burnt.

3.7 Inspection test For the purpose of confirming that test procedures and testers are normal, measure the sulfur content in sulfur reference solution specified in 3.2 (10) to (12) or in sulfur-content reference sample specified in 4.2 (7) by means of this testing method, and compare the measured value with reference value.

When sulfur reference solution gives incomplete combustion, it is advisable to dilute it with light oil having less sulfur (such as *n*-heptane specified in JIS K 2280) and then to burn the diluted solution. The statistical verification method on the reference value and measured value shall follow the description in JIS Z 8402.

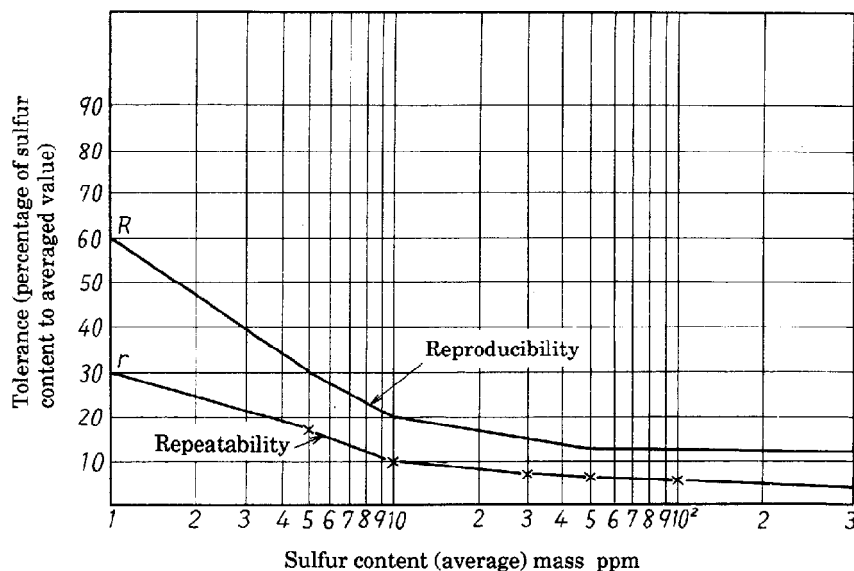
3.8 Precision The tolerance (probability 0.95) of test results measured by oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method shall be as follows.

This precision shall be applied to the sample containing 300 mass ppm or less sulfur.

Remarks: When the test result deviates from the tolerance, it shall be treated according to the description in JIS Z 8402.

- (1) **Repeatability** When the same person carried out test two times with the same sample in the same laboratory using the same tester within successively short time, the tolerance of test results shall be shown in Fig. 3.
- (2) **Reproducibility** When two persons carry out respectively once test with the same sample in different laboratory using different tester, the tolerance of difference between two test results shall be shown in Fig. 3.

Fig. 3. Precision of oxyhydrogen flame combustion-type dimethyl sulfonazo III titration method



3.9 Report of test result On the report of test result, the following items shall be recorded.

- (1) Name of sample, and site and date of sampling

- (2) Standard number of JIS
- (3) Results obtained by the procedures in 3.6
- (4) Items to be specially mentioned

4. Microcoulometric titration-type oxidation method

4.1 Principle of test Introduce sample inside a heated combustion tube, and burn it in a current of oxygen and inert gas. Generate sulfur dioxide by means of combustion, make electrolytic solution absorb the gas, carry out coulometric titration, measure the quantity of electricity spent by the process, and calculate sulfur content.

The sulfur content in sample shall be corrected using a recovery factor which has been obtained in advance by testing sulfur reference solution.

Remarks 1. This test method is suitable for crude oil and petroleum products containing from 1 mass ppm to 1000 mass ppm sulfur.

This test method cannot be applied to the test sample containing 100 mass ppm or over of chlorine, 1000 mass ppm or over of nitrogen, 500 mass ppm or over of heavy metal (for instance, nickel, vanadium, lead), bromine, or iodine.

2. When this test method is applied to the sample containing more than 200 mass ppm of sulfur, it is preferable to dilute the sample with isooctane, toluene, or others to make its concentration about 50 mass ppm.

Informative reference: This method was established on the base of the investigation made by the Japan Petroleum Institute with reference to ASTM D 3120 (Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry).

4.2 Reagents The reagents for microcoulometric titration-type oxidation method shall be as follows.

- (1) Oxygen Specified in JIS K 1101.
- (2) Inert gas Helium or argon with 99.99 or over vol % of purity.
- (3) Electrolytic solution Dissolve specified amount ⁽⁶⁾ of potassium iodide specified in JIS K 8913, sodium azide specified in JIS K 9501, and acetic acid specified in JIS K 8355 in water to make total 1000 ml.

Note ⁽⁶⁾ The amount of each reagent differs depending on the apparatus employed. Table 5 shows an example.

Table 5. Amount of each reagent in electrolytic solution (example)

Name of reagent	Vertical tester	Horizontal tester
Potassium iodide g	5.0	0.5
Sodium azide g	0.5	0.6
Acetic acid ml	6	5

- (4) Sulfur reference solution (250 mass ppm) Weigh 0.98 g of di-*n*-butyl sulfide, containing 21.70 mass % to 21.95 mass % of sulfur, into a 100 ml measuring flask whose mass has been known, to the nearest 0.1 mg, add toluene specified in JIS K 8680 to dissolve it, further add toluene up to the marked line, and measure its mass. Then take its 25 ml into a 250 ml measuring flask with a transfer pipet, and dilute it with toluene up to the marked line.

Calculate the sulfur reference value according to the following formula, and round it off to one decimal place according to JIS Z 8401.

$$A = \frac{0.2187M}{T} \times 10^5$$

where, A : sulfur content in sulfur reference solution (mass ppm)

M : weighed mass of di-*n*-butyl sulfide (g)

T : mass of di-*n*-butyl sulfide and toluene weighed in the 100 ml measuring flask (g)

- (5) Sulfur reference solution (50 mass ppm) Take 20 ml of sulfur reference solution (250 mass ppm) into a 100 ml measuring flask using a transfer pipet, and add toluene specified in JIS K 8680 up to the marked line.

This sulfur reference solution shows the value of $A/5$, and is rounded off to one decimal place.

- (6) Sulfur reference solution (5 mass ppm) Take 2 ml of sulfur reference solution (250 mass ppm) into a 100 ml measuring flask using a transfer pipet, and add toluene specified in JIS K 8680 up to the marked line.

This sulfur reference solution shows the value of $A/50$, and is rounded off to one decimal place.

- (7) Sulfur-content reference sample Sulfur-content reference sample shall be the one whose average and standard deviation of test results, measured in many laboratories (for instance 10 laboratories) on the same sample by microcoulometric titration-type oxidation method, have been obtained.

The average value of these test results shall be made a reference value.

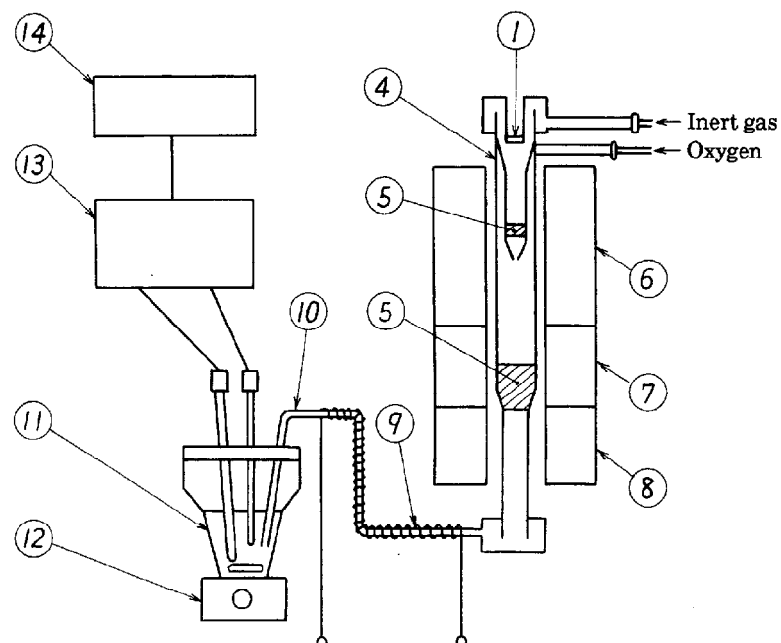
Informative reference: The Japan Petroleum Institute has a standard reference sample, whose sulfur content has been certified on the base of the test results carried out at 10 or more laboratories, therefore it is advisable to use this sample when trueness (a bias) of test results is inspected.

- (8) Water A3 water specified in JIS K 0557.

4.3 Tester for microcoulometric titration-type oxidation method The tester is composed of from (1) to (7), and Fig. 4 shows an example of its construction.

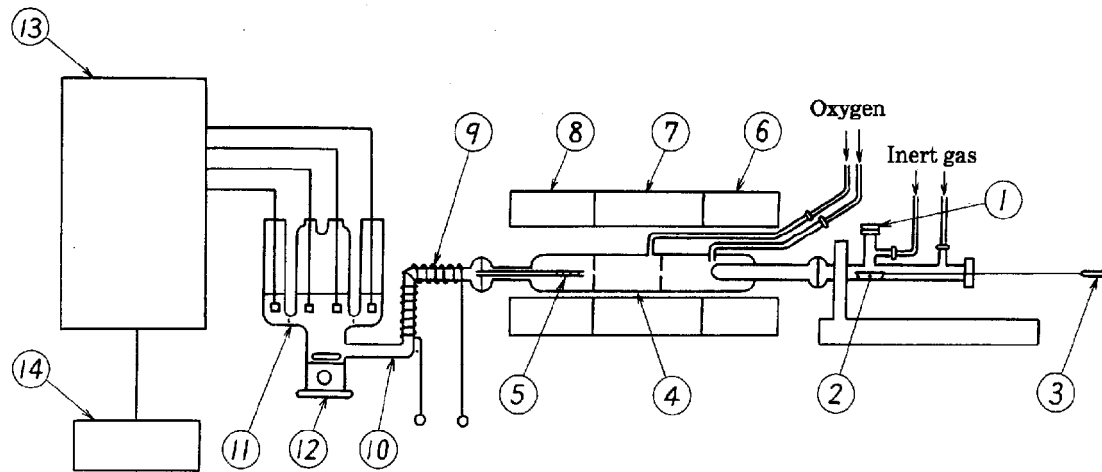
Fig. 4. Construction of tester for microcoulometric titration-type oxidation method

Vertical tester (example)



- | | |
|-------------------------------------|-------------------------------|
| ① Opening for sample injection | ⑨ Tape heater |
| ④ Combustion tube | ⑩ Gas introducing pipe |
| ⑤ Quartz wool | ⑪ Titration cell |
| ⑥ Combustion furnace (entrance) | ⑫ Magnetic stirrer |
| ⑦ Combustion furnace (central part) | ⑬ Microcoulometer |
| ⑧ Combustion furnace (outlet) | ⑭ Indicator of sulfur content |

Horizontal tester (example)



- | | |
|-------------------------------------|-------------------------------|
| ① Opening for sample injection | ⑧ Combustion furnace (outlet) |
| ② Boat for sample | ⑨ Tape heater |
| ③ Shifting rod for sample boat | ⑩ Gas introducing pipe |
| ④ Combustion tube | ⑪ Titration cell |
| ⑤ Quartz wool | ⑫ Magnetic stirrer |
| ⑥ Combustion furnace (entrance) | ⑬ Microcoulometer |
| ⑦ Combustion furnace (central part) | ⑭ Indicator of sulfur content |

- (1) Combustion furnace Capable of controlling separately heating at entrance, central part and outlet.
- (2) Combustion tube Made of quartz and capable of burning sample in oxygen and inert gas flow.
- (3) Titration cell Glass-made cell for electrolyte, equipped with a magnetic stirrer, in which a detecting electrode, reference electrode, and a pair of generating electrodes are built in. The detecting electrode and reference electrode shall be capable of detecting the concentration change of triiodide ion that has generated by absorbing of sulfur dioxide. The generating electrode shall be capable of generating triiodide ion corresponding to the variation of the concentration.
- (4) Microcoulometer This meter successively compares the potential difference, which has been beforehand set between a detecting electrode and reference electrode, with the potential difference between both electrodes during titration, and if discrepancy is found it can provide the current, which will be for compensating this discrepancy, to the generating electrodes.
- (5) Indicator of sulfur content Capable of indicating or recording the sulfur content which has been converted from the electricity supplied into generating electrode (7).

Note (7) Instead, the indicator able to record as integrated value of peak area, may be available.

- (6) Microsyringe With capacity of 10 μl , 20 μl , 50 μl , and 100 μl .
- (7) Boat for sample Made of quartz or platinum.

4.4 Preparation of tester The preparation of tester for microcoulometric titration-type oxidation method shall be as follows.

- (1) Prior to the test, confirm a combustion tube and gas introducing pipe as follows.
- (a) Combustion tube Check the deterioration of quartz and dirt of the combustion tube or quartz wool, and if not clean, clean it or exchange, and then carry out sufficient pre-burn.
- (b) Gas introducing pipe Check the deterioration and dirt on it, and if there found, clean it.

- (2) Wash inside a titration cell with electrolyte, and put the electrolyte enough to dip each electrode.

- (3) Connect each terminal of a detecting electrode, reference electrode, and generating electrode to the circuit of a microcoulometer ⁽⁸⁾.

Note ⁽⁸⁾ In case of a vertical tester, set the potential of end point at this step.

- (4) Connect the gas introducing pipe of a titration cell to the end of combustion tube outlet, apply electric power to a tape heater, and keep the gas introducing pipe of the titration cell at 100°C or higher.
- (5) Set measuring conditions of such as flow rate of oxygen and inert gas, temperature of combustion furnace, and microcoulometer. An example of measuring conditions are shown in Table 6.

Table 6. Measuring conditions (example)

Item			Vertical tester	Horizontal tester
Flow rate of oxygen		ml/min	320	160
Flow rate of inert gas		ml/min	80	40
Temperature of combustion furnace	Entrance	°C	850	700
	Central part	°C	950	900
	Outlet	°C	300	800
Micro-coulometer	Bias voltage	mV	—	160
	Potential of end point	mV	250	—
	Gain		2 or 3 scales	Low (about 200)

4.5 Measurement of recovery factor The measurement of recovery factor of the microcoulometric titration-type oxidation method shall be carried out as follows depending on sulfur content.

- (1) Choose one of the sulfur reference solutions in Table 7, which corresponds to approximate value of sulfur content in sample, and take the quantity shown in Table 7 using a microsyringe.

Table 7. Type and quantity of sulfur reference solution to be taken

Approx. value of sulfur content in sample mass ppm	Type	Taken quantity μl	
		Vertical tester	Horizontal tester
1 or over to and excl. 10	Sulfur reference solution (mass 5 ppm)	50 to 100	10 to 30
10 or over to and excl. 100	Sulfur reference solution (mass 50 ppm)		5 to 10
100 or over up to and incl. 300	Sulfur reference solution (mass 250 ppm)	20 to 50	2 to 5

- (2) Introduce the sulfur reference solution taken in the microsyringe into a combustion tube according to the following method.
- (a) Vertical tester Insert the needle point of the microsyringe up to the entrance of the combustion tube through the opening for sample injection, inject $1.0 \mu\text{l/s}$ to $1.2 \mu\text{l/s}$ ⁽⁹⁾ of sulfur reference solution, and read accurately ⁽¹⁰⁾ quantity of the injected solution.
- (b) Horizontal tester Have the needle point of a microsyringe pierce the opening for sample injection, inject sulfur reference solution into a sample boat, and read accurately ⁽¹⁰⁾ quantity of the injected solution. Then shift the sample boat just in front of the entrance of a combustion tube, hold it as it is for 20 s to 60 s ⁽¹¹⁾, and send it at the entrance of the combustion tube.

Notes ⁽⁹⁾ In order to uniformly inject sample, it is convenient to use either a dispenser or auto-injector.

⁽¹⁰⁾ Inhale the same amount of air into the microsyringe before and after the injection of sulfur reference solution, read the injected quantity making use of difference of readings, and the accurate value can be obtained owing to the correction of the quantity likely evaporated from needle point.

⁽¹¹⁾ If the sample boat is inserted without holding in front of the entrance of a combustion tube, incomplete combustion of sample may give inaccurate measurement.

Remarks: In case of employing a horizontal tester, when a direct injection of sulfur reference solution is made, follow the procedures in (a). Provided that the injecting rate shall be $0.2 \mu\text{l/s}$ to $0.3 \mu\text{l/s}$.

- (3) Read the value on the indicator of sulfur content, calculate the recovery factor according to the following formula, and round it off to two decimal places according to JIS Z 8401.

$$F = \frac{B}{V \cdot D \cdot C_s}$$

where, F : recovery factor
 B : quantity of sulfur ⁽¹²⁾ (ng)
 V : injected quantity of sulfur reference solution (μl)
 D : 0.866 g/cm³ (density of sulfur reference solution)
 C_s : sulfur reference value in sulfur reference solution (mass ppm)

Note ⁽¹²⁾ When the tester records integrated value of peak area, convert it into the sulfur quantity (ng) according to the following formula.

$$B = \frac{1.99S}{R}$$

where, B : quantity of sulfur (ng)
 S : integrated value of peak area
 R : set value by range switch of microcoulometer (Ω)

- (4) Measure repeatedly recovery factor, average 3 stable measurements which are successively measured and are staying from 0.65 to 0.95, make it the averaged recovery factor ⁽¹³⁾, and use it for calculation of sulfur content in sample.

Note ⁽¹³⁾ If the averaged recovery factor doesn't fall in this range, reprepare sulfur reference solution and retry the measurement.

If retried measurement doesn't fall in this range, check the tester and method of procedures.

Remarks: The confirmation of the averaged recovery factor to be carried out during measurement shall be done in every series of measurements, and when one series of measurements exceeds 4 h, carry it out at every 4 h.

If the difference between the averaged recovery factor obtained at Note ⁽¹³⁾ and the confirmed is over 0.05, obtain again the averaged recovery factor.

- (5) Measure sulfur content in sulfur-content reference sample, and confirm that the test result, which has been calculated making use of the averaged recovery factor obtained at (4), falls within [reference value ± 3 × standard deviation (standard sample)]. When the result exceeds this limit, check the tester and carry out again the procedures shown in (4).

Remarks: The statistical verification method for trueness shall preferably make reference to JIS Z 8402.

4.6 Measurement of sample The measurement of sample shall be as follows.

- (1) Sampling method Carry out sampling according to the primary sampling method and the secondary sample preparation method specified in JIS K 2251 or to the method corresponding to this.
- (2) Procedures for measurement The procedures for measurement shall be as follows.
 - (a) Case of making direct measurement Take sample in a microsyringe by the quantity shown in Table 7 depending on the approximate sulfur content in sample, introduce it into a combustion tube according to the procedure in 4.5 (2), and read the value given on the indicator of sulfur content. Repeat twice this procedure on the same sample.
 - (b) Case of making measurement after dilution Weigh accurately sample to the nearest 1 mg, dilute it with isooctane or toluene to get about 50 mass ppm, and prepare diluted sample solution. When the sample doesn't show complete dissolution, toluene only can be available. Carry out the same procedures on this diluted sample solution as in (a), and measure sulfur content.

Informative reference: The sample, whose approximate sulfur content is less than 200 mass ppm, is suitable for direct measurement, and the sample, more than 200 mass ppm, is suitable for the measurement after dilution.

4.7 Calculation and precision

4.7.1 Calculation The calculation of microcoulometric titration-type oxidation method shall be as follows.

- (1) Case of direct measurement of sample Use the read value at 4.6 (2), and calculate sulfur content to whole number or less according to the following formula.

$$S = \frac{B}{V \cdot D \cdot F}$$

where, *S*: sulfur content (mass ppm)
 B: amount of sulfur ⁽¹²⁾ (ng)
 V: injected quantity of sample (μl)
 D: density of sample ⁽¹⁴⁾ (g/cm³)
 F: averaged recovery factor

Note ⁽¹⁴⁾ In advance, measure it at room temperature according to JIS K 2249.

- (2) Case of measurement after dilution Use the read value at 4.6 (2), and calculate sulfur content to whole number or less according to the following formula.

$$S = \frac{B \cdot G}{V \cdot H \cdot F}$$

where, S : sulfur content (mass ppm)
 B : amount of sulfur (¹²) (ng)
 G : whole quantity of diluted sample solution (ml)
 V : injected quantity of sample (μl)
 H : weighed amount of sample (g)
 F : averaged recovery factor

- (3) When two results calculated according to (1) or (2) fall within the tolerance by repeatability in Table 8, average them, and round it off to a whole number according to JIS Z 8401. If it falls out of the tolerance by repeatability, retry the procedures in 4.6 (2).

4.7.2 Precision The tolerance (probability 0.95) of test results measured by microcoulometric titration-type oxidation method shall be as follows.

Remarks: When the test result deviates from the tolerance, it shall be treated according to the description in JIS Z 8402.

- (1) **Repeatability** When the same person carries out test two times with the same sample in the same laboratory using the same tester within successively short time, the tolerance of test results shall be shown in Table 8.
- (2) **Reproducibility** When two persons carry out respectively once test with the same sample in different laboratory using different tester, the tolerance of difference between two test results shall be as shown in Table 8.

Table 8. Precision of microcoulometric titration-type oxidation method

Unit: mass ppm		
Sulfur content	Repeatability	Reproducibility
1 or over to and excl. 10	1	2
10 or over to and excl. 30	2	4
30 or over up to and incl. 1000	0.067S	0.133S

S : Average of test results

4.8 Report of test result On the report of test result, the following items shall be recorded.

- (1) Name of sample, and site and date of sampling
- (2) Standard number of JIS
- (3) Results obtained by the procedures in 4.7.1
- (4) Items to be specially mentioned

5. Combustion tube-type air method

5.1 Principle of test Introduce air into a quartz-made combustion tube heated at 950°C to 1100°C, and make sample burn. Make hydrogen peroxide solution (3%) absorb the sulfur oxide that has generated, to prepare sulfuric acid, titrate this sulfuric acid to make it neutral with sodium hydroxide standard solution, and find the sulfur content.

Remarks: This testing method is suitable for determination of sulfur content contained in crude oil or petroleum by 0.01 mass % or more, but not for the sample treated with additives containing the following.

- (1) Metals forming insoluble sulfate (such as barium or calcium)
- (2) Elements forming acids when it was burnt (such as phosphorus, nitrogen or chlorine)

Informative reference: This method has been established on the base of the investigation carried out by the Japan Petroleum Institute.

5.2 Reagents The reagents for combustion tube-type air method shall be as follows.

- (1) Hydrogen peroxide solution (3%) Dilute one volume of hydrogen peroxide solution (30%) specified in JIS K 8230 with 9 volumes of water. Store this solution in a brown colored bottle.
- (2) 0.05 mol/l sodium hydroxide standard solution Dissolve about 2 g of sodium hydroxide specified in JIS K 8576 in water to make total 1000 ml. Store it in a brown colored bottle equipped with a protecting tube packed with soda lime in order not to absorb carbon dioxide in air.

The standardization of this solution shall be carried out as follows.

- (a) Weigh accurately 1 g to 1.25 g of dried sulfamic acid specified in JIS K 8005 to the nearest 0.1 mg, dissolve in water, and make total 250 ml by using a 250 ml measuring flask.
- (b) Take 25 ml aliquot of sulfamic acid solution prepared at (a) into an Erlenmeyer flask using a transfer pipet, drip bromothymol blue indicator solution specified in JIS K 8001, and titrate it with sodium hydroxide solution. Make it an end point when the solution turns blue from yellow, find the quantity of sodium hydroxide solution needed for titration, calculate the concentration of sodium hydroxide standard solution according to the following formula, and round it off to four decimal places according to JIS Z 8401.

$$N = \frac{1.030A}{V}$$

where, N : concentration of sodium hydroxide standard solution (mol/l)

A : weighed mass of sulfamic acid (g)

V : quantity of sodium hydroxide solution needed
for titration (ml)

Remarks: In case of sample containing less sulfur, use 0.02 mol/l
sodium hydroxide standard solution.

- (3) Mixed indicator ⁽¹⁵⁾ Mix the following two solutions with the same volume. Store this solution in a brown colored bottle, and never use the one elapsed for one week or longer.

Note ⁽¹⁵⁾ Instead of mixed indicator, 0.1% solution of methyl purple may be available.

(a) Dissolve 0.125 g of methyl red specified in JIS K 8896 in 100 ml of ethanol (95) specified in JIS K 8102.

(b) Dissolve 0.083 g of methylene blue (dihydrate) specified in JIS K 8897 in 100 ml of ethanol (95).

- (4) Active carbon Granular active carbon

- (5) Sulfuric acid (1 + 1) Add 50 ml of sulfuric acid specified in JIS K 8951 into 50 ml of water.

This adding of sulfuric acid shall be carried out slowly while stirring water.

- (6) Sodium hydroxide solution Dissolve 30 g of sodium hydroxide specified in JIS K 8576 in 100 ml of water.

- (7) Sulfur-content reference sample Sulfur-content reference sample shall be the one whose average and standard deviation of test results (within the tolerance of reproducibility), measured in many laboratories (for instance, 10 laboratories) on the same sample by combustion tube-type air method, have been obtained.

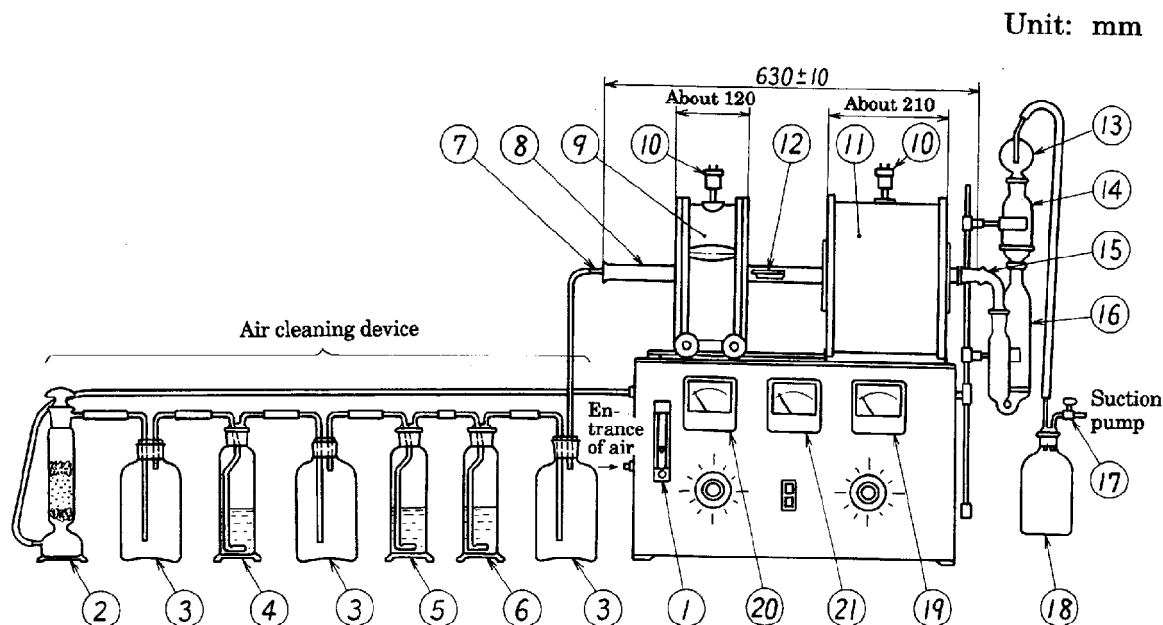
The average value of these test results shall be made a reference value.

Informative reference: The Japan Petroleum Institute has a reference sample, whose sulfur content has been certified on the base of the test results carried out at 10 or more laboratories, therefore it is advisable to use this reference sample when trueness (a bias) of test results is inspected.

- (8) Water A3 water specified in JIS K 0557.

5.3 Tester for combustion tube-type air method The tester is composed of from (1) to (11), and Fig. 5 shows an example of its construction.

Fig. 5. Construction of tester for combustion tube-type air method (example)



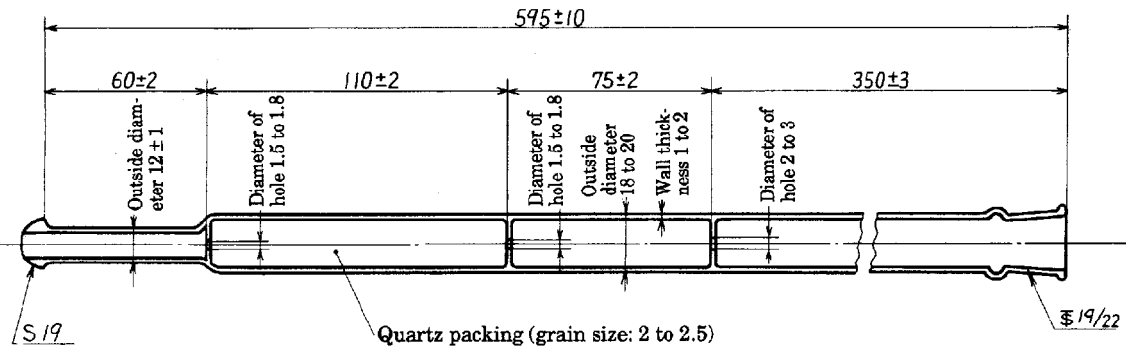
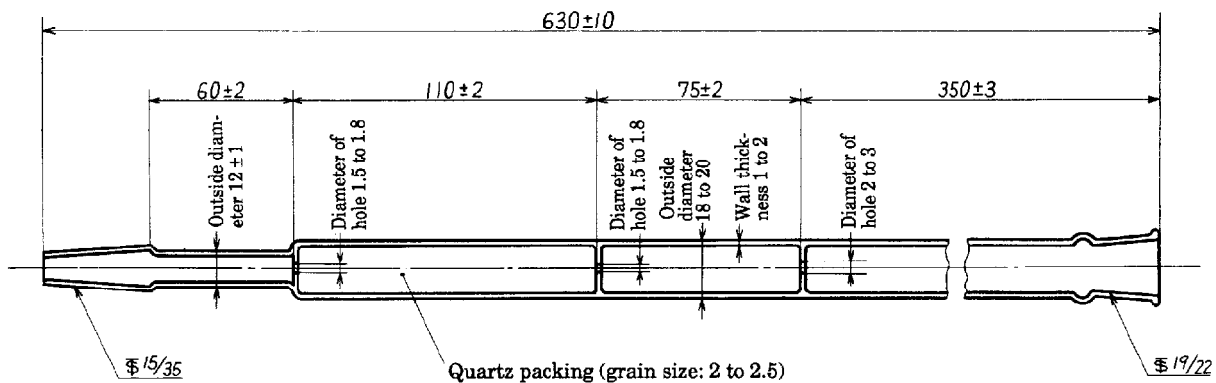
- | | |
|--|---|
| ① Flowmeter | ⑫ Boat |
| ② Bottle for active carbon | ⑬ Trap |
| ③ Empty bottle | ⑭ Upper absorption tube |
| ④ Washing bottle (sulfuric acid) | ⑮ Adapter |
| ⑤ Washing bottle (sodium hydroxide solution) | ⑯ Lower absorption tube |
| ⑥ Washing bottle (water) | ⑰ Flow-rate control cock |
| ⑦ Stopper | ⑱ Empty bottle for suction |
| ⑧ Combustion tube (made of quartz) | ⑲ Indicative thermoelectric thermometer (for stationary electric furnace) |
| ⑨ Electric furnace (movable) | ⑳ Indicative thermoelectric thermometer (for movable electric furnace) |
| ⑩ Thermocouple | ㉑ Ammeter |
| ⑪ Electric furnace (stationary) | |

- (1) Combustion tube Made of transparent quartz glass, and with shape and dimensions as shown in Fig. 6.

Remarks: Fig. 154 specified in JIS K 2839 corresponds to this.

Fig. 6. Combustion tube for combustion tube-type air method (example)

Unit: mm

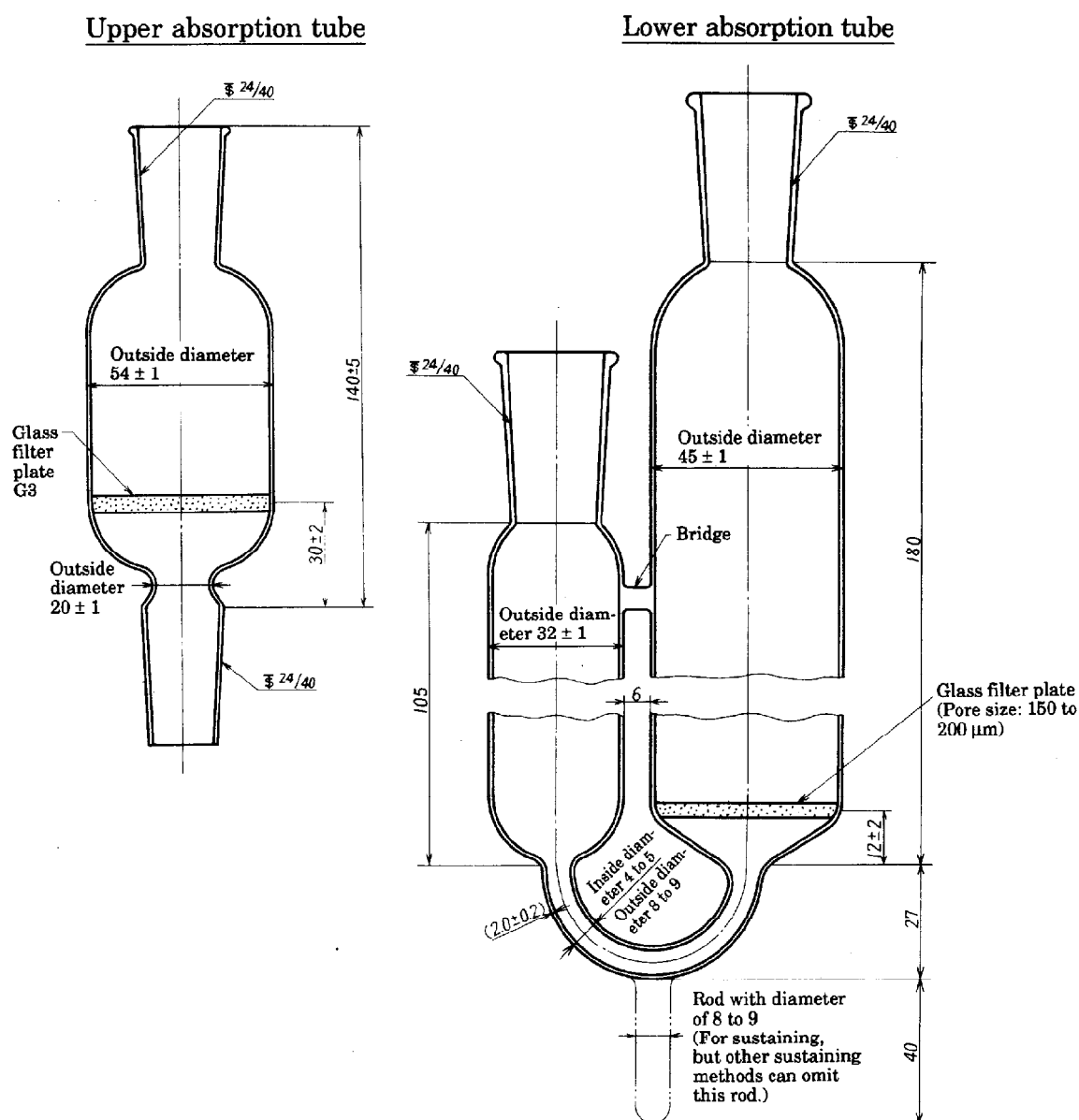
(1) Spherically ground joint(2) Taper ground joint

- (2) Absorption tube Made of borosilicate glass 1 specified in JIS R 3503, and with shape and dimensions as shown in Fig. 7.

Remarks: Fig. 64 and Fig. 79 specified in JIS K 2839 correspond to this.

Fig. 7. Absorption tube for combustion tube-type air method

Unit: mm



- (3) **Trap** Made of borosilicate glass 1 specified in JIS R 3503, and capable of connecting with absorption tube through a conical ground joint. Its example is shown in Fig. 8.

Remarks: Fig. 65 specified in JIS K 2839 corresponds to this.