

JIS

JAPANESE INDUSTRIAL STANDARD

Liquid petroleum products — Testing method of components

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**Business Department,
Japanese Standards Association**
4-1-24, Akasaka, Minato-ku,
Tokyo, JAPAN 107
TEL. 03-3583-8002
FAX. 03-3583-0462

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JAPANESE INDUSTRIAL STANDARD

J I S

Liquid petroleum products —
Testing method of components

K 2536-1996

1. **Scope** This Japanese Industrial Standard specifies the method to determine the hydrocarbons contained in liquid petroleum products by means of fluorescent-indicator adsorption method after classifying them into three hydrocarbon-types i.e. saturated hydrocarbons, olefin hydrocarbons, and aromatic hydrocarbons; and specifies the method to determine benzene, toluene, xylene, methanol, methyl tertiarybutyl ether (hereafter referred to as "MTBE"), etc. in gasoline by means of a gas chromatography.

- Remarks
1. This Standard may involve hazardous chemicals, operations and equipment. This Standard does not purport to specify all of the problems associated with safety during use. Therefore the user of this test method shall determine the regulatory limitations on safety and health, prior to the tests.
 2. The standards cited in this Standard are shown in Attached Table 1.
 3. The corresponding International Standard to this Standard is shown in Table 1.
 4. The units and numerical values given in { } in this Standard are based on the traditional units and are appended for informative reference.

Table 1. Corresponding International Standard to this testing method

Name of testing method	Corresponding International Standard
Fluorescent-indicator adsorption method	ISO 3837: 1993 (Liquid petroleum products — Determination of hydrocarbon types — Fluorescent indicator adsorption method)

2. **Definitions** For the purpose of this Standard the following principal definitions apply:

- (1) **hydrocarbon types** Three types such as saturated hydrocarbons (hereafter referred to as "saturated components"), olefin hydrocarbons (hereafter referred to as "olefins"), and aromatic hydrocarbons (hereafter referred to as "aromatics").
- (2) **saturated hydrocarbons** Total of alkanes (carbons are bonded straightly or in branches) and cycloalkanes (carbons are bonded in ring-shape).

Remarks: Alkane and cycloalkane are called "paraffin hydrocarbon" and "naphthene hydrocarbon", respectively.

- (3) **olefins** Total of alkenes (carbons are bonded straightly or in branches including one double bond) and dienes (carbons are bonded including 2 double bonds).

2
K 2536-1996

- (4) aromatics Total of aromatic hydrocarbons and aromatic olefin hydrocarbons of single-ring or multi-rings.
- (5) C₅ and lower distillate This means the hydrocarbons of C₅ and lower which are the distillate collected in the receiver when the product is distilled in accordance with Annex 1.
- (6) C₆ and higher distillate This means the hydrocarbons of C₆ and higher which are the residual remained in the flask when the product is distilled in accordance with Annex 1.
- (7) kerosines In this test method, this means the amount calculated by multiplying total amount (vol%) of *n*-tridecane and *n*-tetradecane by factor 14.
- (8) total components Total components are the generic term of the components which are contained in the product by 0.1 vol% or over when measured by all components testing method by gas chromatography.

3. Classification of testing methods Testing methods are classified into 5 classes as shown in Table 2.

Table 2. Classification of testing methods

Classification	Target hydro-carbon type and components	Application	Unit in test result	Kind of applicable oil	Number of clause
Fluorescent-indicator adsorption method	Saturated hydrocarbons Olefins Aromatics	Applicable to liquid petroleum products of which end point is 315°C or lower ⁽¹⁾ .	vol%	Automobile gasoline Aircraft gasoline Fuel for aircraft turbine engine Kerosine	4.
Aromatic testing method by gas chromatography	Aromatics Benzene Toluene Xylene	Applicable to liquid petroleum products of which end point is 220°C or lower ⁽¹⁾ .	Mass % or vol%	Reformed gasoline Automobile gasoline Aircraft gasoline	5.
Total components testing method by gas chromatography	Total components Benzene Toluene Xylene Methanol MTBE Kerosines	Applicable to liquid petroleum products of which end point is 250°C or lower ⁽¹⁾ .		Reformed gasoline Automobile gasoline	6.
Component testing method by tandem type gas chromatography	Benzene Toluene Xylene Methanol MTBE Kerosines			vol%	Automobile gasoline
Testing method for compound containing oxygen by gas chromatography	Methanol MTBE				8.

Note (1) The end point is based on the determination of distillation characteristics under ordinary pressure specified in JIS K 2254.

- Remarks 1. When there is any doubt about the test results of methanol, MTBE, benzene, and kerosines which are obtained by respective tests in Table 2, the result obtained from the total component testing method by gas chromatography in 6. adjusted by using the reference gasoline for component in 6.3 (6) (b) shall be taken.
2. For measurement of methanol, MTBE, benzene and kerosines, gas chromatography according to respective test methods in Table 2 may be used.

Further, when there is any doubt about those test results, the result obtained from the total component testing method by gas chromatography in 6. adjusted by using the reference gasoline for component in 6.3 (6) (b) shall be taken.

3. In the case of fluorescent-indicator adsorption method for samples containing pentane (C_5) and lower hydrocarbons, the tests in Annex 1 and Annex 2 are carried out.

Informative reference: Fluorescent-indicator adsorption method is sometimes called "FIA method".

4. Fluorescent-indicator adsorption method

4.1 Principle of test Inject 0.75 mL of sample in the adsorption tube in which very fine silica gel and silica gel with attached little fluorescent dyestuff are packed. After all the sample has been adsorbed on the silica gel, add 2-propanol to desorb the sample, flow down to the bottom of the adsorption tube, and develop it. The hydrocarbon components are separated into aromatics, olefins, and saturated hydrocarbon according to the difference in adsorbing affinity.

The fluorescent dyestuff is also separated together with each hydrocarbon component, and the boundary between individual hydrocarbon types can be judged using an ultraviolet lamp. The concentrations (vol%) of aromatics, olefins, and saturated hydrocarbons are calculated by measuring the length of respective layers given at the measuring part of the adsorption tube. In the case of a sample containing C_5 and lower distillate carry out the procedures shown in Annex 1 (Taking an aliquot of pentane and lower distillate) and Annex 2 (Gas chromatographic analysis of pentane and lower distillate).

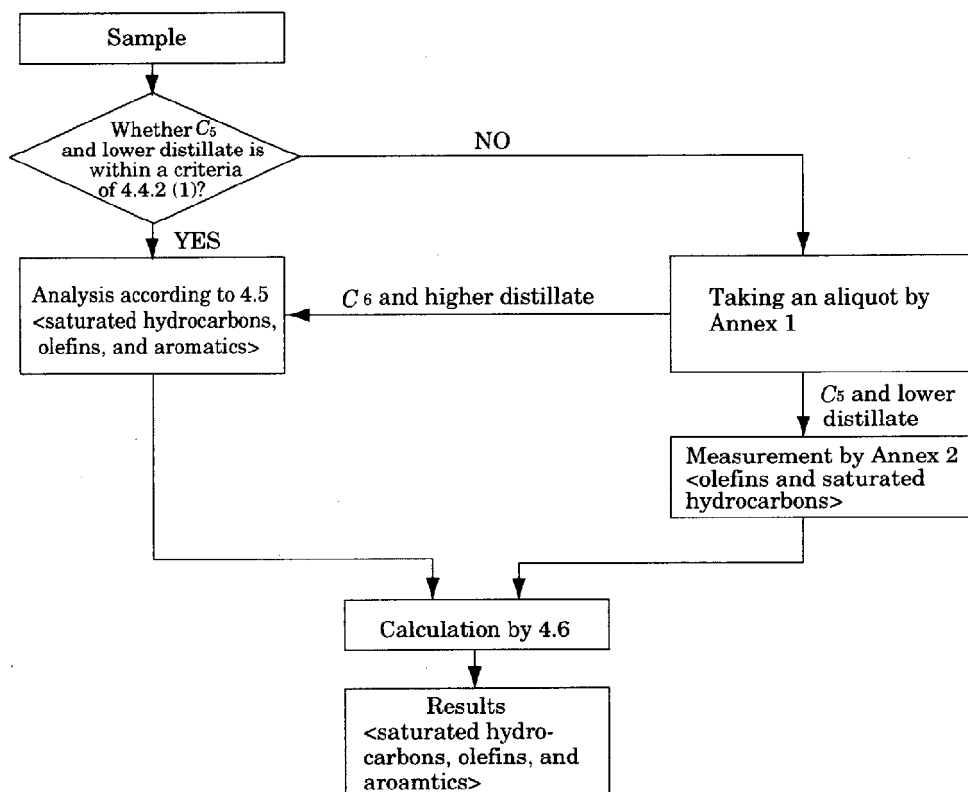
- Remarks 1. This test method is applied to measurement of 5 vol% to 99 vol% of aromatics, 0.3 vol% to 55 vol% of olefins, and 1 vol% to 95 vol% of the saturated hydrocarbons.
2. For analyses of hydrocarbon types, the instrumental analysis method by gas chromatography or the like may be used. The instrumental analysis method shall be used after confirming no significant difference from the results obtained by this test method in accordance with the provisions of JIS Z 8402.

If there is any doubt about the test result obtained by the instrumental analysis, the test results obtained by the test method in this Standard shall be taken.

3. When a sample containing alcohols and ethers is measured by fluorescent indicator adsorption method, relative ratio of the hydrocarbon types from which the alcohols and ethers are removed can be obtained.

Informative reference (1) The process of fluorescent indicator adsorption method is shown in Informative reference Fig. 1.

Informative reference Fig. 1. Process of fluorescent indicator adsorption method



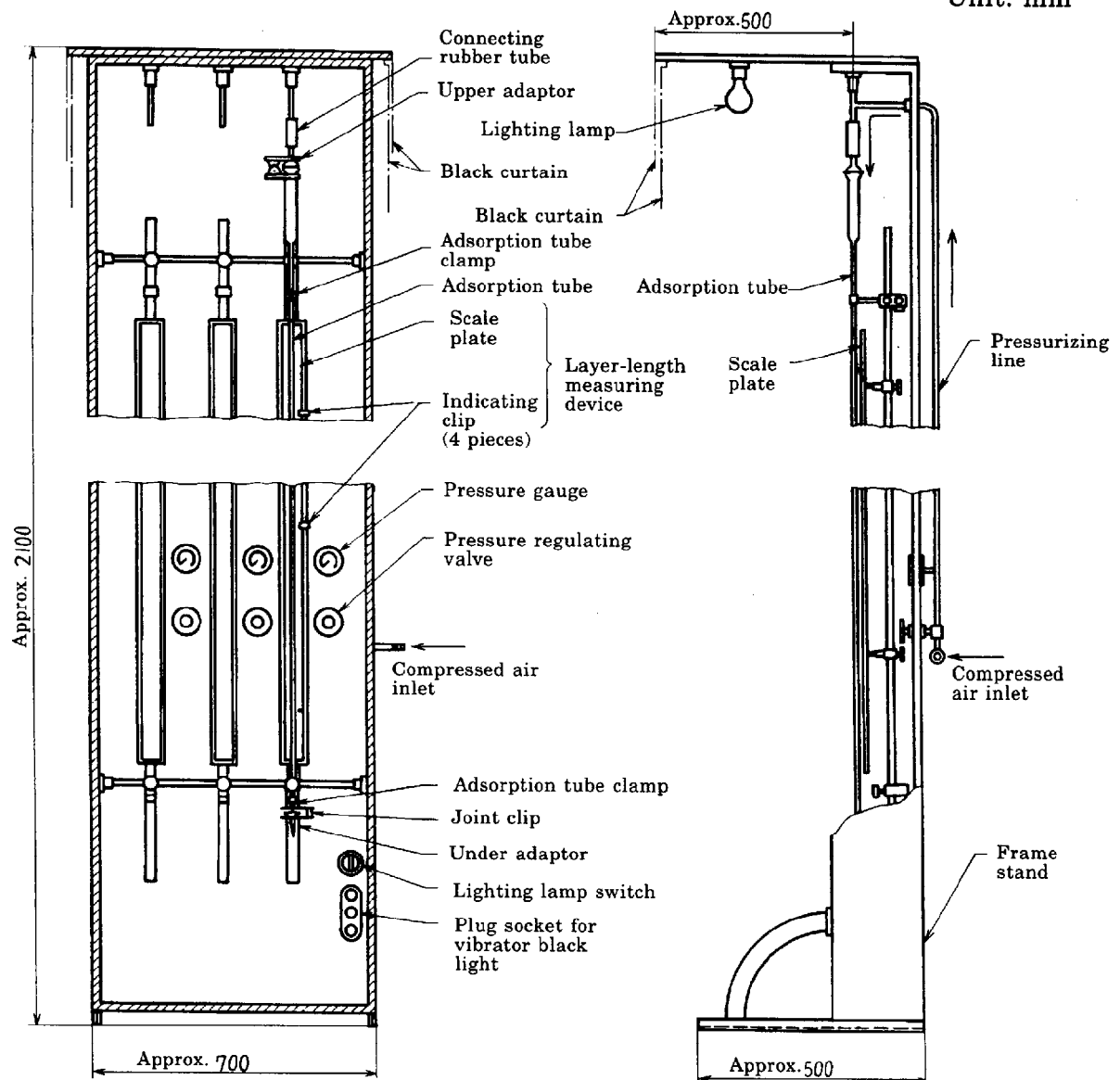
- (2) In order to check the accuracy (bias) about test results, it is preferable to use the reference sample for FIA which has been certified by the Japan Petroleum Institute.

Statistical dealing of accuracy can be done with reference to the description in JIS Z 8402.

4.2 Fluorescent indicator adsorption tester The tester is constructed as shown in Fig. 1, and composed of the following (1) to (7).

Fig. 1. Fluorescent indicator adsorption tester (an example)

Unit: mm



- (1) Adsorption tube Type II adsorption tube is shown in Fig. 2.

Remarks: The method to inspect the dimension of measuring part of the adsorption tube shall be as follows.

- (1) Inspection for inside diameter Place mercury in the measuring part, and calculate the inside diameter according to the following formula:

$$D = 2 \sqrt{\frac{W}{3.14 \times l \times p}}$$

where, D : inside diameter (cm)

W : mass of mercury (g)

l : length of mercury column at measuring part (cm)

p : density of mercury at the temperature for measurement (g/cm^3)

- (2) Inspection for uniformity of inside diameter Place mercury in the measuring part by the length of about 100 mm, measure its length while shifting its location, and the difference between the longest and the shortest must be not more than 0.3 mm.

- (2) Upper adaptor Upper adaptor is shown in Fig. 3.
- (3) Layer-length measuring device The device consists of the scale plate with 800 mm to 1200 mm length equipped with 4 movable metal indication clips and of a holding plate for the scale plate, and the example of its construction is shown in Fig. 4.

Fig. 2. Type II adsorption tube

Unit: mm

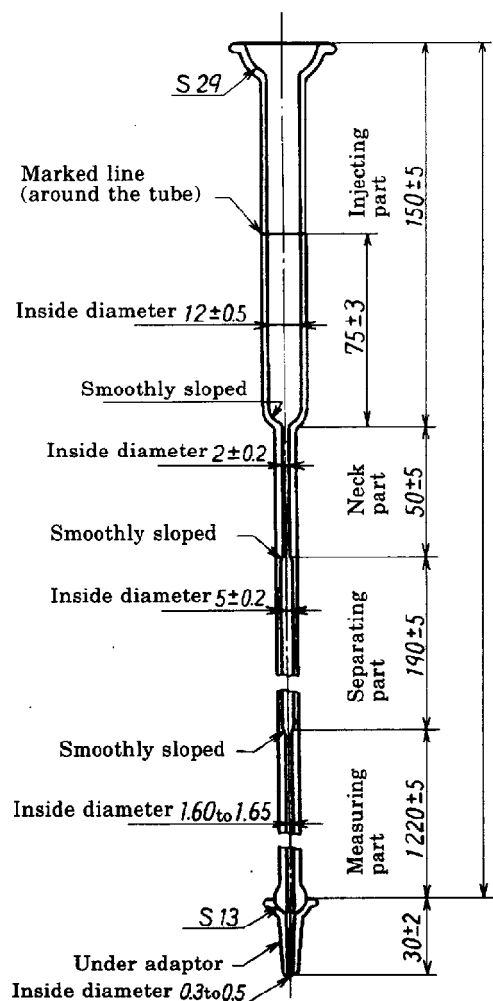


Fig. 3. Upper adaptor

Unit: mm

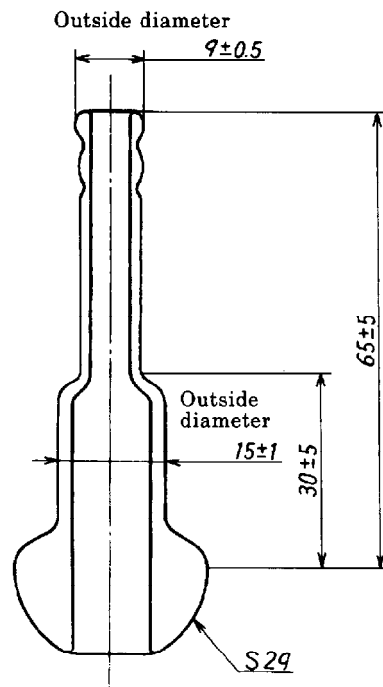
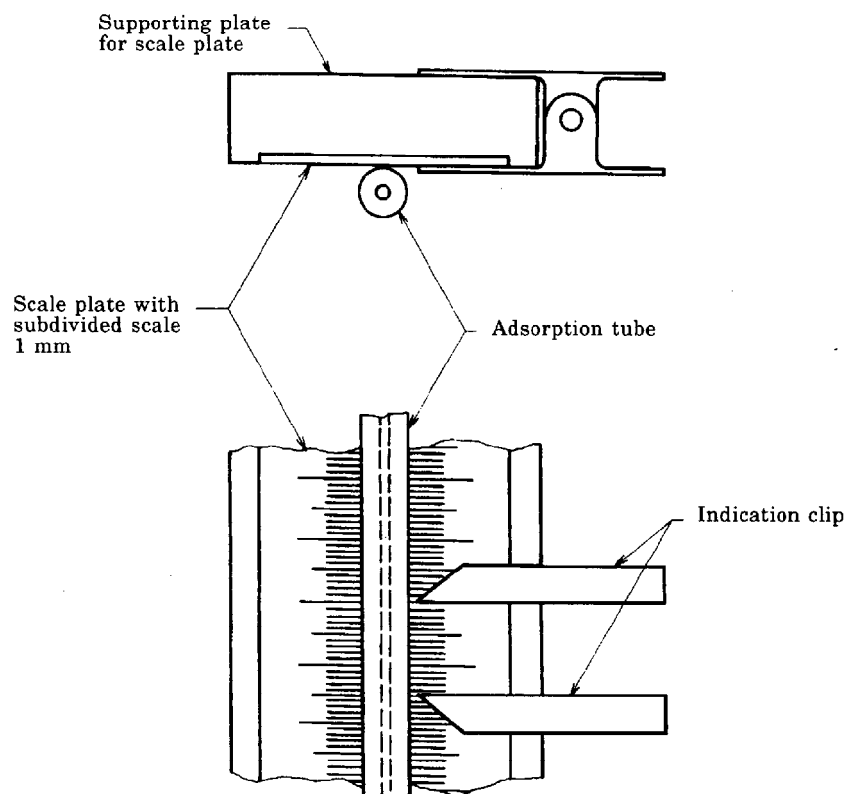


Fig. 4. Layer-length measuring device (an example)



- (4) **Light source** Mercury lamp with filter ⁽²⁾ or suitable ultraviolet light source, which can emit the light of wavelength near 365 nm.

Note ⁽²⁾ HF100 specified in JIS C 7604 is suitable.

Informative reference: Occasionally, an ultraviolet light source is perpendicularly fixed along the adsorption tube.

- (5) Electric vibrator A vibrator suitable for filling silica gel in the adsorption tube.
- (6) Syringe The syringe consists of an injection cylinder with 1 mL capacity and scale interval of 0.01 mL or 0.02 mL, and of a needle measuring about 100 mm in length and 1 mm in outside diameter; and the material of the needle is stainless steel.
- (7) Pressurizing apparatus It shall be equipped with a pressure regulating valve and pressure gauge and the like for arbitrarily controlling the pressure within the range of 0 kPa to 103 kPa {0 kgf/cm² to 1.05 kgf/cm²} when applying pressure after attaching pressure-proof rubber tube to the upper adaptor of the adsorption tube.

4.3 Reagents Reagents shall be as follows.

- (1) Silica gel This shall be prepared so as not to polymerize olefin hydrocarbons as far as possible, and shall comply with the requirements in Table 3. Prior to use, put it in a shallow dish, and dry at $176 \pm 5^\circ\text{C}$ for 3 h. Transfer this dried silica gel into a desiccator while it is hot, and keep it from moisture in air.

Table 3. Specification of silica gel

Surface area		430 m ² /g to 530 m ² /g
pH of 5% water-slurry		5.5 to 7.0
Ignition loss at 955°C		4.5 mass % to 10.0 mass %
Iron content (as Fe ₂ O ₃)		50 mass ppm max.
Sieve test	Standard sieve nominal size μm	Amount passed the sieve %
	180	100
	150	95 min.
	75	15 max.

Remarks: For measurement of pH of 5 % water-slurry, weigh out 5 g of silica gel into a 250 mL beaker, add 100 mL of water, and stir for 20 min with a magnetic stirrer. Thereafter measure it.

Informative reference: For the measurement of the surface area, referring to ASTM D 3663 is preferable.

- (2) Silica gel with attached fluorescent dyestuff This shall be the silica gel to which fluorescent dyestuff such as petrol red AB4, olefin dyestuff, and aromatic dyestuff are adsorbed, or the silica gel with attached fluorescent dyestuff on the market. This silica gel with attached fluorescent dyestuff shall be stored in a dark place with closely stoppered. Even while storing under such conditions, the effect of fluorescent dyestuff may be lost after long period (for instance, 6 months or longer), therefore it is advisable to test its performance using the sample having definite components.

Informative reference: The silica gel with attached fluorescent dyestuff, prepared by E. Merck company in Germany and UOP company in USA, can be used as the silica gel with fluorescent dyestuff on the market.

- (3) 2-propanol The 2-propanol specified in JIS K 8839.
- (4) Water Water specified as A3 in JIS K 0557.
- (5) Acetone The acetone specified in JIS K 8034.
- (6) Compressed gas Air or nitrogen of which the pressure can be adjusted to be in the range 0 kPa to 103 kPa (0 kgf/cm² to 1.05 kgf/cm²) at the upper part of the adsorption tube.

4.4 Preparation for test

4.4.1 Sampling and preparation of sample The sample shall be sampled and prepared according to the sampling method of a primary sample and the preparation method of a secondary sample which are specified in JIS K 2251, otherwise the method similar thereto.

4.4.2 Preparation of sample When the sample is expected to contain alcohol or ether, it shall be preliminarily confirmed that the sample does not contain them by any one of the test methods stated in 6., 7. and 8., and then the procedures stated in (1) and (2) below shall be carried out.

Remarks: In case of petroleum products containing MTBE, measure MTBE by any one of the test methods stated in 6., 7. and 8.

- (1) Group the following samples into C₅ and lower distillate and C₆ and higher distillate according to Annex 1, and use the C₆ and higher distillate as the sample for 4.5.
 - (a) When the sample contains light hydrocarbon of C₃ and lower.
 - (b) When the sample contains C₄ hydrocarbon by 5 vol% or more.
 - (c) When the sample contains C₄ and C₅ hydrocarbons by 10 vol% or more, in total.
 - (d) When existence of C₅ and lower hydrocarbon in the sample is uncertain.

Remarks: Dark coloring of the sample may make it difficult to read the borderline in the procedure of 4.5. In such a case, remove coloring substance according to the determination of distillation characteristics at ordinary pressure specified in JIS K 2254, and use it as the sample for 4.5.

- (2) The C₅ and lower distillate separately taken from the sample of C₅ and lower distillate shall be submitted to the sample for Annex 2 (3).

Note (3) If the gas chromatographic analysis specified in Annex 2 shows that the concentration of C_6 and higher hydrocarbons, accompanying with C_5 and lower distillate, is 3 or more vol% which has been calculated on the base of the sample before distilling C_5 and lower distillate, separative distilling according to Annex 1 shall be re-tried.

In the case of the sample containing MTBE, it gives a peak on the retention time for C_6 and higher hydrocarbons, therefore it shall not be misunderstood as that of saturated hydrocarbons.

4.4.3 Site for installation of tester In order to make it easy to observe the borderline between hydrocarbon types, install the tester in a dark room or a room where darkness is controllable.

4.4.4 Preparation of adsorption tube The preparation of adsorption tube shall be as follows:

- (1) Suspend the dried adsorption tube by the clamp which has been fixed just below the upper adaptor in the injection portion.
- (2) Place a net made of phosphor bronze or copper (74 μm), measuring 6 mm in diameter, at the center of ground place of the under adaptor, and connect it with the measuring part of the adsorption tube, in order to prevent silica gel from dropping. Align both the under adaptor and the adsorption tube while packing silica gel and carrying out procedures thereafter.
- (3) Add bit by bit silica gel from the injection portion through a glass funnel. Pour the silica gel uniformly up to half of the separation part while holding the measuring part of the adsorption tube with a hand and moving a vibrator along lengthwise direction of the adsorption tube. Stop the vibrator, and add the silica gel with attached fluorescent dyestuff to make its thickness 3 mm to 5 mm. Then supplement the silica gel while vibrating the adsorption tube by the vibrator, and fill silica gel firmly to a height of 75 mm in the injection portion. To make the silica gel uniform, give vibration for about 4 min to the adsorption tube using the vibrator (4).

Note (4) Uneven filling of silica gel affects the test result.

Remarks: When silica gel is filled to the adsorption tube, static electricity sometimes gives unevenness of filling, so wipe outside the adsorption tube with a moistened cloth.

- (4) Fix vertically the adsorption tube filled with silica gel on the frame stand.

4.5 Procedures of test The procedures of test shall be as follows:

- (1) Cool the sample and syringe at 2°C to 4°C .
- (2) Put the sample (0.75 ± 0.03 mL) in a syringe and inject it to a point about 30 mm lower from the surface of silica gel filled in the injection portion of the adsorption tube.

- (3) Fill 2-propanol⁽⁵⁾ specified in 4.2 (3) up to the spherically ground place of the injecting portion, connect the upper adaptor to the adsorption tube, apply pressure of 14 kPa {0.14 kgf/cm²} for 2.5 min, and then increase the pressure up to 34 kPa {0.35 kgf/cm²} for 2.5 min to make the liquid flow down. Then, after about 1 h, adjust pressure⁽⁶⁾ so that the measurements in (4) are possible, and thereafter do not carry out pressure control.

Notes ⁽⁵⁾ In the case of the sample the majority of which distills out at 205°C or higher, 3-methyl-1-butanol may sometimes give superior elution.

⁽⁶⁾ The pressure of 28 kPa to 69 kPa {0.29 kgf/cm² to 0.70 kgf/cm²} is suitable for the sample of gasoline, and 69 kPa to 103 kPa {0.70 kgf/cm² to 1.05 kgf/cm²} for the sample of aircraft turbine fuel, but this pressure differs according to the filling condition of silica gel and the molecular weight of sample.

- (4) When a red band between 2-propanol layer and aromatics layer progresses about 350 mm from the top of the measuring part, mark promptly borderlines between layers of saturated hydrocarbons, olefins, and aromatics, using indicating clips under ultraviolet light⁽⁷⁾, from the lowest end (the lowest of wetted zone) according to the criteria for borderlines shown in Table 4, measure the length of each layer to the nearest 1 mm, and record them. If the total length of every layer is 500 mm or less, either unsuitable filling of silica gel or incomplete separation is supposed, therefore retry the test.

Note ⁽⁷⁾ Be careful since ultraviolet light is harmful.

Remarks: The liquid petroleum products containing alcohols or ethers give shorter developed layers proportionally to the amount mixed. In this case, retry the test after increasing the amount of sample.

- (5) In order to make less the error caused by the movement of borderline while marking, when the red band lowers further by about 50 mm, measure, in the contrary order to (4), the length of each layer from uppermost end to the nearest 1 mm, and record them.
- (6) Obtain the mean value of the lengths of each layer read in the procedures of (4) and (5) to one decimal place.
- (7) Remove pressure of the adsorption tube, detach the upper adaptor, and extract the silica gel from the adsorption tube by using a capillary tube. Then, clean the inside of the adsorption tube with water and acetone, and dry it by passing compressed gas.

Informative reference: It is convenient for extraction of the used silica gel to use the stainless steel-made capillary tube of 1 mm to 1.5 mm outside diameter and about 1.5 m length the tip of which is so machined as to make civil water flow therethrough.

Table 4. Criteria of borderline

Measuring part	Hydrocarbon type	Boundary judging criteria	Fluorescence color of each layer
Up		Upper end of red band ⁽⁸⁾	Red band
	Aromatics	Lowest end of clear blue fluorescence color ⁽⁹⁾	Clear blue layer Thin blue layer
	Olefins	Lowest end of strongest part of yellow fluorescence color	Yellow layer
	Saturated hydrocarbons	Lowest end of sample (lowest wetted part)	Colorless
Down			Intensity of fluorescence

Notes ⁽⁸⁾ Such sample as cracked gasoline often gives an obscure brown color instead of red band, but this should be considered because of aromatics.

⁽⁹⁾ If blue fluorescence (by aromatics) is not found, the red or brown band is supposed to be a part of the under layer (by olefins or, if no olefins, by saturated hydrocarbons) which can be clearly distinguished.

Informative reference:

Since yellow fluorescence differs according to silica gel with fluorescent dyestuff to be used, and that of UOP Co.-make is stronger in fluorescence than that of Merck Co.-make, when the yellow strongest part does not exist, it should not be misunderstood as the boundary between olefins and saturated hydrocarbons.

4.6 Calculation and precision

4.6.1 Calculation Employing each layer length of aromatics, olefins, and saturated hydrocarbons, which has been measured in 4.5 (6), and the measured values obtained in Annex 1 and Annex 2, calculate the concentration (vol%) of aromatics, olefins, and saturated hydrocarbons according to the formulas stated below, and round off the concentration of each component to the first decimal place according to the requirements specified in JIS Z 8401.

When the total concentration of aromatics, olefins, and saturated hydrocarbons does not give 100 vol%, adjust the measured value of the component with the higher concentration to make 100 vol%.

(1) Case of liquid petroleum products not containing alcohols and ethers

(a) When separation procedure of C_5 and lower distillate is not carried out

$$A = \frac{L_a}{L} \times 100$$

$$O = \frac{L_o}{L} \times 100$$

$$S = \frac{L_s}{L} \times 100$$

where, A : volumetric percentage of aromatics (vol%)
 O : volumetric percentage of olefins (vol%)
 S : volumetric percentage of saturated hydrocarbons (vol%)
 L_a : length of aromatics layer (mm)
 L_o : length of olefins layer (mm)
 L_s : length of saturated hydrocarbons layer (mm)
 L : $L_a + L_o + L_s$ (mm)

(b) When separation procedure of C_5 and lower distillate is carried out

$$A = \frac{L_a}{L} \times H$$

$$O = \frac{L_o}{L} \times H + (100 - H) \times \frac{G_o}{100}$$

$$S = \frac{L_s}{L} \times H + (100 - H) \times \frac{G_s}{100}$$

where, H : yield of C_6 and higher distillate (vol%) (refer to Annex 1)
 G_o : volumetric percentage of olefins in C_5 and lower distillate (vol%) (refer to Annex 2)
 G_s : volumetric percentage of saturated hydrocarbons in C_5 and lower distillate (vol%) (refer to Annex 2)

(2) Case of liquid petroleum products containing MTBE

(a) When separation procedure of C_5 and lower distillate is not carried out

$$A = \frac{L_a}{L} \times (100 - M)$$

$$O = \frac{L_o}{L} \times (100 - M)$$

$$S = \frac{L_s}{L} \times (100 - M)$$

where, A : volumetric percentage of aromatics (vol%)
 O : volumetric percentage of olefins (vol%)
 S : volumetric percentage of saturated hydrocarbons (vol%)
 L_a : length of aromatics layer (mm)
 L_o : length of olefins layer (mm)
 L_s : length of saturated hydrocarbons layer (mm)
 L : $L_a + L_o + L_s$ (mm)
 M : volumetric percentage of MTBE measured by any testing method in 6., 7. and 8. (vol%)

(b) When separation procedure of C_5 and lower distillate is carried out

$$A = \frac{L_a}{L} \times [H - M + (100 - H) \times \frac{G_m}{100}]$$

$$O = \frac{L_o}{L} \times [H - M + (100 - H) \times \frac{G_m}{100}] + (100 - H) \times \frac{G_o}{100}$$

$$S = \frac{L_s}{L} \times [H - M + (100 - H) \times \frac{G_m}{100}] + (100 - H) \times \frac{G_s}{100}$$

where, H : yield of C_6 and higher distillate (vol%) (refer to Annex 1)
 G_o : volumetric percentage of olefins in C_5 and lower distillate (vol%) (refer to Annex 2)
 G_s : volumetric percentage of saturated hydrocarbons in C_5 and lower distillate (vol%) (refer to Annex 2)
 G_m : volumetric percentage of MTBE in C_5 and lower distillate (vol%)

Remarks: When liquid petroleum products containing alcohols and ethers (excepting MTBE) are measured, total of the value of hydrocarbon types obtained by fluorescent indicator adsorption method and the value of the alcohols and ethers measured by the other test method (the test method in 6. or the like) shall be adjusted to 100 vol%.

If the alcohols and ethers are not measured, total sum of hydrocarbon types shall be adjusted to 100 vol%. In this case, it shall be appended that the value is the concentration of the hydrocarbon types excepting the alcohols and ethers.

4.6.2 **Precision** The tolerance (probability 0.95) on the test results obtained in this test method is as stated below.

Remarks 1. If test result falls out the tolerance, follow the requirements specified in JIS Z 8402.

2. In the case of liquid petroleum products containing alcohols and ethers, the precision is not applied.

- (1) **Repeatability** When the tests are carried out twice successively in a short time, in the same laboratory, by the same person, using the same apparatus and on the same sample, the allowable difference between test results shall be as shown in Table 5.
- (2) **Reproducibility** When two tests are carried out in different laboratories, by different persons, using different apparatus, on the same sample, once in each situation, the allowable difference between two test results shall be as shown in Table 5.

Table 5. Precision

Unit: vol%

Hydrocarbon types	Concentration	Repeatability	Reproducibility
Aromatics	5	0.7	1.5
	15	1.2	2.5
	25	1.4	3.0
	35	1.5	3.3
	45	1.6	3.5
	50		
	55		
	65	1.5	3.3
	75	1.4	3.0
	85	1.2	2.5
	96	0.7	1.5
	99	0.3	0.7
Olefins	1	0.4	1.7
	3	0.7	2.9
	5	0.9	3.7
	10	1.2	5.1
	15	1.5	6.1
	20	1.6	6.8
	25	1.8	7.4

Table 5. (continued)

Unit: vol%

Hydrocarbon types	Concentration	Repeatability	Reproducibility
Olefins (continued)	30	1.9	7.8
	35	2.0	8.2
	40		8.4
	45		8.5
	50	2.1	8.6
	55	2.0	8.5
Saturated hydrocarbons	1	0.3	1.1
	5	0.8	2.4
	15	1.2	4.0
	25	1.5	4.8
	35	1.7	5.3
	45		5.6
	50		
	55		
	65		5.3
	75	1.5	4.8
	85	1.2	4.6
	95	0.3	2.4

4.7 Report of test results The following items shall be stated on the test result.

- (1) Name of sample, sampling site, and date of sampling
- (2) Standard number of this JIS
- (3) Names of test items and results obtained by 4.6.1
- (4) Particulars

5. Gas chromatography

5.1 Principle of test Making use of a capillary column (hereafter referred to as "column") on which polar stationary-phase liquid has been applied, elute aromatics in the sample selectively from the components such as saturated hydrocarbons and olefins. Detect this using a hydrogen flame ionization detector, and record a chromatogram and an integrated value of peak area. Identify each aromatic hydrocarbon in comparison with the chromatogram on which each component has been known, calculate the concentration (mass%) of benzene, toluene, xylene (including ethyl benzene) and other aromatic hydrocarbons by an internal standard method, and sum up their concentrations to find aromatics.

Remarks: This test method is applied to the measurement of benzene, toluene, xylene, and aromatics each of which shows 0.1 mass% (vol%) or over.

Informative references (1) This test method is the method prepared originally in Japan by employing the method studied by the Japan Petroleum Institute (used column TCEP) and informative reference method No. 23 of Center Laboratory of Customer, Ministry of Finance (used column PEG-20M).

(2) By using the TCEP column of this test method and changing the test conditions in Table 7, methanol, MTBE, and kerosines, as well as aromatic hydrocarbons, can be measured.

5.2 Tester and instrument

5.2.1 Gas chromatograph This apparatus consists of main components shown in the following (1) to (5). The structural requirements other than those mentioned here shall follow the requirements specified in JIS K 0114.

- (1) Sample introducing part This is a introducing part of split type attachable to a column, and capable of keeping its temperature at 230°C to 250°C.
- (2) Column vessel It shall be kept at 40°C to 250°C with allowable limits of $\pm 0.5^\circ\text{C}$.
- (3) Column A quartz or stainless steel capillary to the inside of which TCEP [1,2,3-tris (2-cyanoethoxy) propane] or PEG-20M (polyethylene glycol-20M) is applied or chemically combined as polar stationary-phase liquid. An example is shown in Table 6.

Table 6. Column (an example)

Stationary-phase liquid		TCEP	PEG-20M
Inside diameter	mm	0.22	0.25
Length	m	50	30
Film thickness of liquid phase	μm	0.42	0.25

- (4) Detector and detector vessel Detector shall be a flame ionization detector, and the vessel be kept at the same or higher temperature than that of the column.
- (5) Data processor It shall record not only chromatogram but also the duration of each peak, the integrated value of peak area, and the rate (%) of it to the total integrated value of peak areas.

5.2.2 Microsyringe Use a suitable capacity one (1 μL to 10 μL) according to the introducing amount of sample.

In the case of 1 μL syringe, a wire must go through to the tip of its needle and it shall completely introduce whole amount that has been taken into the apparatus.

5.3 Reagents Reagents shall be as follows:

- (1) cis-decalin Purity of 99 mass% or superior one.
- (2) n-undecane Specified in JIS K 0509.
- (3) Benzene Specified in JIS K 8858.
- (4) Toluene Specified in JIS K 8680.
- (5) Ethylbenzene Purity of 99 mass% or superior one.
- (6) 1,2,4-trimethylbenzene Purity of 99 mass% or superior one.
- (7) n-butylbenzene Purity of 99 mass% or superior one.
- (8) 2,2,4-trimethylpentane Specified in JIS K 9703.
- (9) Helium or nitrogen Helium with purity of 99.9 vol% or superior one, or nitrogen specified in JIS K 1107.
- (10) Hydrogen Specified in JIS K 0512.
- (11) Methane Purity of 50% or higher.

5.4 Preparation of test

5.4.1 Adjustment of gas chromatograph The adjustment of a gas chromatograph shall be as follows:

- (1) Connect the column to the specified position of the gas chromatograph.
- (2) Open the main valve of a carrier-gas bomb and the pressure regulator of bomb side, and adjust secondary pressure to 0.5 MPa to 0.9 MPa {5 kgf/cm² to 9 kgf/cm²}. Then, open gradually a carrier-gas regulating valve of gas chromatograph side and a flow rate regulator, control to keep total flow rate at sample introducing part to 70 mL to 100 mL per minute, and record the flow rate.
- (3) Let the carrier gas flow into the column at a rate of 0.5 mL to 0.8 mL per minute.
- (4) In order to send quickly the eluted component to detector from the column outlet, flow the same gas as carrier gas in the column outlet at a rate of 30 mL to 50 mL per minute.

Remarks: Apply soapy water on each connecting part of column and piping to confirm if there is no leakage of carrier gas.

- (5) Turn on electric source of the gas chromatograph, open the cover of a column vessel, and make the temperature inside of the column vessel room temperature.
- (6) Make pass hydrogen and air as the fuel gas and ignition improver gas for the flame ionization detector. Immediately, ignite the gas at the burning nozzle of the detector using an igniter.

Informative references (1) In this procedure, setting of some excess hydrogen gas and a little less air provides easy ignition. To confirm if the gas is ignited, set a mirror at detector outlet, and observe the cloudiness on the mirror caused by steam produced.

(2) Set the flow rates of hydrogen and air most suitable for the gas chromatograph employed. When the flow rates of hydrogen and air are changed, reconfirm if the burning continues or not.

- (7) Keep the temperature of sample introducing part and in the detector vessel to a constant arbitrary temperature from 230°C to 250°C.
- (8) Turn on the power source of the data processor, and set the condition required for measuring the integrated value of peak area.

5.4.2 Setting of test condition The setting of test conditions shall be as follows:

- (1) After setting the temperature condition in the column vessel according to Table 7, run the temperature increasing mechanism in the column vessel and the data processor, and confirm if the base line of the data processor is stabilized ⁽¹⁰⁾.

Note ⁽¹⁰⁾ Set the whole width of peak output of the data processor to 1 mV, then confirm that fluctuation of the base line is not more than 0.01 mV during about 10 min.

Informative reference: When a column is first used, detector may be contaminated by the light-weighted impurities in stationary-phase liquid or the residual solvent which elutes out during pre-burning of the column, therefore to prevent the contamination, keep the upper limit of service temperature of the column (for instance, 130°C for TCEP, and 210°C for PEG-20M) for 1 h to 2 h without immediately connecting the detector to outlet of column.

After allowing to cool at a room temperature, connect the outlet of the column to the detector, and confirm that the base line has got stability similarly to (1).

- (2) In order to get the separatory performance similar to the chromatogram (an example) indicated in Fig. 5 ⁽¹¹⁾ or Fig. 6 ⁽¹¹⁾, set the test conditions by adjusting the flow rate of carrier gas, split ratio and the like. Table 7 shows an example of test conditions.

Table 7. Test conditions (an example)

Stationary-phase liquid		TCEP	PEG-20M
Carrier gas	Kind	Helium	Helium
	Inlet flow rate mL/min	100	80
	Linear velocity cm/s	22.5	27
	Split ratio	200:1	100:1
Temperature in column °C		80→130	40 (retain for 4 min)→ 210 (retain for 5 min)
Rate of temperature rise °C/min		1 to 2	4
Temperature at introducing part °C		250	230
Temperature at detector °C		250	230
Quantity of introduced sample µL		0.1 to 0.5	0.1 to 0.5

Note (1) Some sample may elute benzene and toluene before the elution of saturated hydrocarbons and olefins will finish, and make an overlap on them, therefore it is necessary to confirm that the peaks of benzene and toluene belong to that of simple component using a chromatogram.

Informative reference Confirmation of split ratio When the separation on a chromatogram is not adequate, it is advisable to measure and confirm the split ratio according to the following method:

- (1) After completion of adjusting gas chromatograph according to 5.4.1, confirm if the base line of the chromatogram has stabilized according to 5.4.2 (1).
- (2) Take 2 µL to 3 µL of methane in a 10 µL microsyringe, immediately introduce it into the gas chromatograph, and run promptly a data processor.
- (3) At the moment when the peak of methane is detected, output the retention time. Calculate the linear velocity and split ratio of carrier gas from the retention time according to the following formulas. If no peak of methane is detected, carry out the procedures in (1) to (3) again after confirming that the flame of the hydrogen flame ionization detector is still kept and there is no leakage of carrier gas around column connecting place.

$$S = \frac{L}{T}$$

$$R = S \times (D/2)^2 \times \pi \times 60$$

$$S_p = \frac{F}{R}$$

where, S : linear velocity (cm/s)
 L : length of column (cm)
 T : retention time of methane (s)
 R : flow rate of carrier gas (mL/min)
 D : inside diameter of column (cm)
 S_p : split ratio (ratio of sample-inlet flow rate to column flow rate)
 F : flow rate at sample inlet part (mL/min)
 π : ratio of circumference of circle to its diameter (3.14)

Fig. 5. Chromatogram of cracked gasoline by TCEP column (an example)

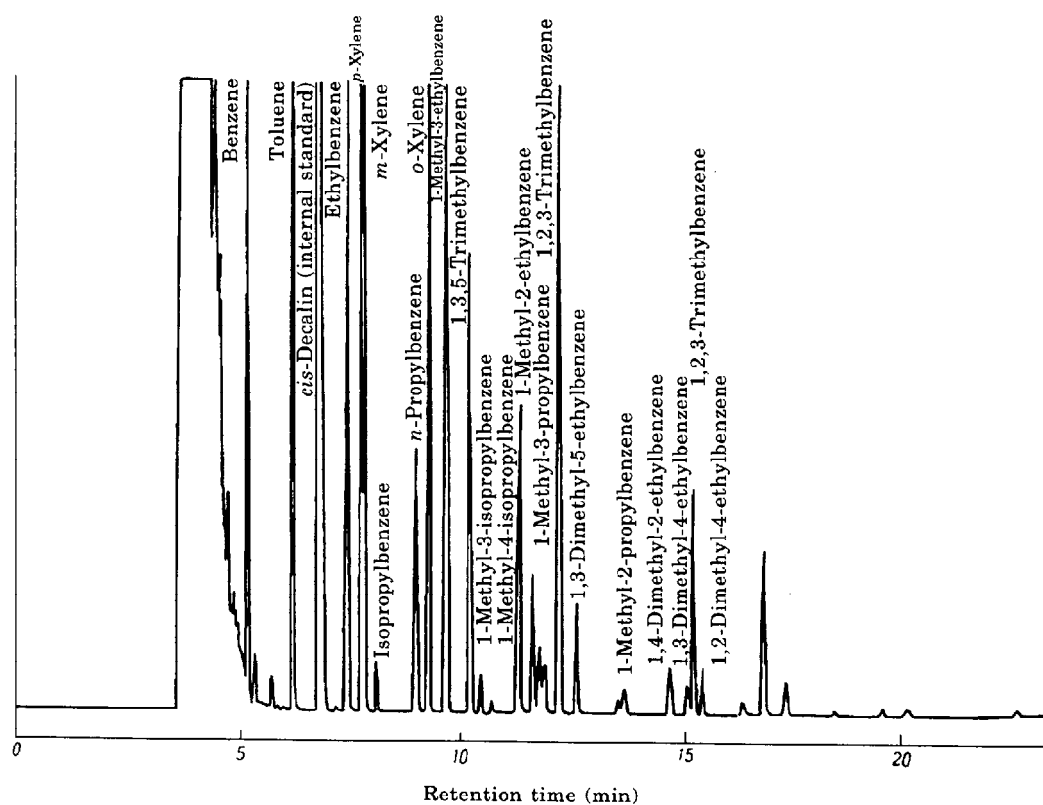
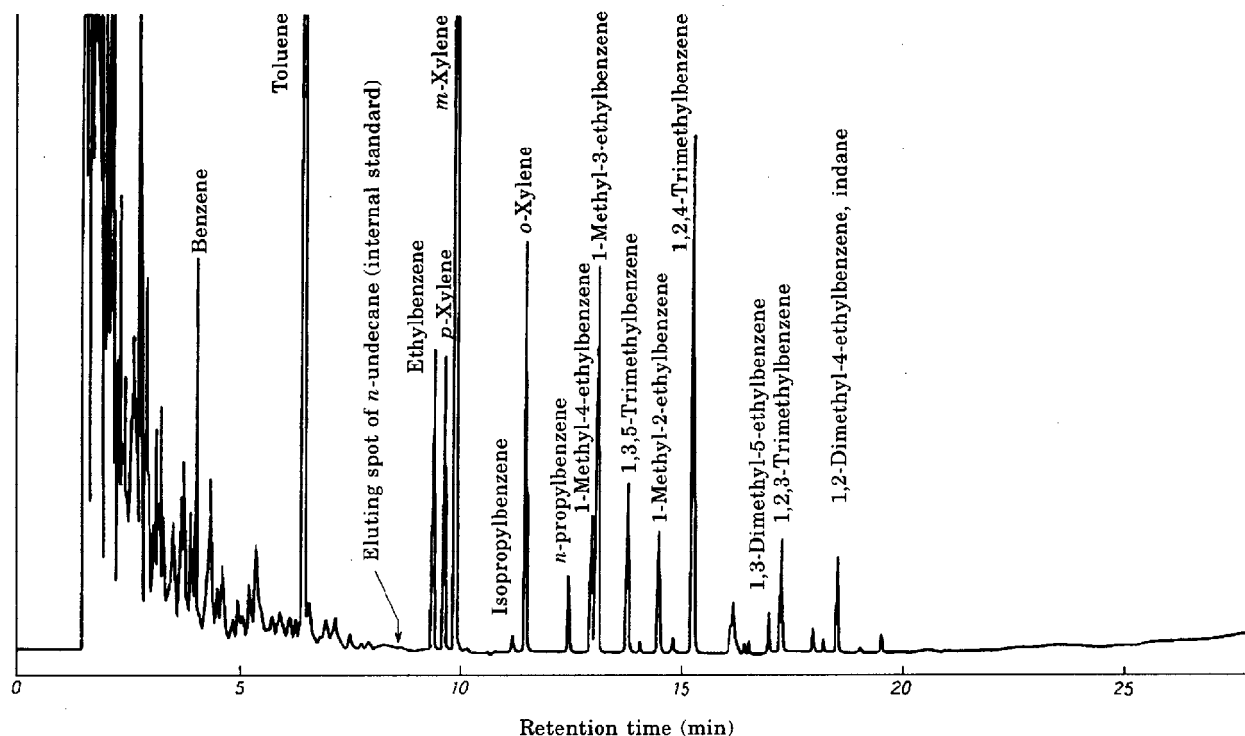


Fig. 6. Chromatogram of cracked gasoline by PEG-20M column (an example)



5.4.3 Measurement of mass relative sensitivity The measurement of mass relative sensitivity shall be as follows:

- (1) Preparation of relative sensitivity measuring sample Weigh out the hydrocarbons shown in Table 8, successively in the order of higher boiling point to the nearest 1 mg into a 50 mL Erlenmeyer flasks with a stopper ground commonly, and prepare about 20 g relative sensitivity measuring sample. Calculate concentration (mass%) of each hydrocarbon component in the relative sensitivity measuring sample, and round them off to the fourth decimal place according to requirements specified in JIS Z 8401.

Table 8. Relative sensitivity measuring sample

Hydrocarbon	Mixing ratio (mass%)	Order to mix
Internal standard material (<i>cis</i> -decalin, <i>n</i> -undecane)	5	①
<i>n</i> -Butylbenzene	5	②
1,2,4-Trimethylbenzene	5	③
Ethylbenzene	5	④
Toluene	5	⑤
Benzene	5	⑥
2,2,4-Trimethylpentane	70	⑦

Remarks: Internal standard material shall be *cis*-decalin for the column using TCEP as stationary-phase liquid, and *n*-undecane for the column using PEG-20M as stationary-phase liquid.

- (2) Measurement of mass relative sensitivity for aromatic components This measurement shall be carried out according to (a) to (c).

Remarks: When benzene, toluene, and xylene are obtained, this operation shall be necessarily carried out. When aromatics (total of aromatic components) are obtained, the mass relative sensitivity given in Table 9 may be used.

- (a) Take 0.1 µL to 0.2 µL of relative sensitivity measuring sample in a 1 µL microsyringe, immediately introduce it into the sample inlet part of the gas chromatograph, and promptly run the temperature-rising mechanism of the column vessel and the data processor.
- (b) When whole hydrocarbon in relative sensitivity measuring sample is eluted out and a recording of chromatogram is completed, output the integrated value of peak area.
- (c) Repeat 3 times or more the procedures in (a) and (b), calculate the mass relative sensitivity to the third decimal place according to the following formula, obtain the average, and round it off to the second decimal place according to the requirements specified in JIS Z 8401.

$$f_{iw} = \frac{A_i / M_i}{A_s / M_s}$$

- where,
- f_{iw} : mass relative sensitivity depending on aromatic hydrocarbon *i* contained in relative sensitivity measuring sample
 - A_i : integrated value of peak area of aromatic hydrocarbon *i* contained in relative sensitivity measuring sample
 - M_i : concentration of aromatic hydrocarbon *i* contained in relative sensitivity measuring sample (mass%)
 - A_s : integrated value of peak area of internal standard material
 - M_s : concentration of internal standard material (mass%)

Table 9. Mass relative sensitivity of aromatic components

Name of component	Mass relative sensitivity by TCEP method	Mass relative sensitivity by PEG-20M method
Benzene	1.09	1.06
Toluene	1.08	1.06
<i>p</i> -Xylene	1.00	1.04
<i>m</i> -Xylene	1.00	1.04
<i>o</i> -Xylene	1.00	1.04
Ethyl benzene	1.06	1.04
1,2,4-Trimethylbenzene	1.03	1.03
<i>cis</i> -Decalin	1.00	—
<i>n</i> -Undecane	—	1.00

5.5 Procedures of test

5.5.1 Sampling and preparation of sample The sample for the test shall be sampled and prepared according to the sampling method of a primary sample and the preparation method of a secondary sample which are specified in JIS K 2251, otherwise the method similar to it.

5.5.2 Direct measurement of sample The direct measurement of sample shall be carried out as follows:

- (1) Take 0.1 μ L to 0.5 μ L of the sample, previously cooled in a refrigerator or the like, in a 1 μ L microsyringe, introduce promptly it into the gas chromatograph which has been set at the test condition achieved in 5.4.2 (2), immediately start the temperature-rising mechanism of the column vessel and the data processor, and record chromatogram and integrated value of peak area.
- (2) Confirm existence or nonexistence of the peak of retention time which corresponds to used internal standard material (*cis*-decalin or *n*-undecane) and ethyl benzene. If the sample whose retention time is the same as that of the internal standard material is contained, correct as shown in Note ⁽¹²⁾ when calculation is carried out.

5.5.3 Measurement of added internal standard sample After direct measurement of the sample, the measurement of added internal standard sample shall be carried out as follows:

- (1) Take 0.4 g of internal standard material into a flask of about 20 mL with a stopper ground in common, and weigh its mass to the nearest 1 mg. Add 8 mL of sample in this, weigh its mass to the nearest 1 mg, and mix them to be the test sample. Prepare the test sample at every measuring.

Remarks: If prepared test sample is not immediately tested, preserve it in a refrigerator.

- (2) Sample 0.1 μL to 0.5 μL of the test sample preliminarily cooled in a refrigerator into a 1 μL microsyringe, introduce promptly into the gas chromatograph, and immediately start the temperature-rising mechanism of column vessel and the data processor.

Remarks: The quantity of test sample to be introduced shall be previously decided adequately answering to the concentration of aromatics. For example, it is preferable to introduce 0.1 μL for 50 % of aromatics concentration, and 0.5 μL for 1 %.

- (3) After all hydrocarbons in the sample are eluted and the recording of chromatogram is finished, output the integrated value of peak area.
- (4) Identify the component of aromatic hydrocarbons shown in the sample which has been plotted on the chromatogram by referring the chromatogram of Fig. 5 (an example) when TCEP column is used, and the chromatogram of Fig. 6 (an example) when PEG-20M column is used.
- (5) If there is individual aromatic hydrocarbon that can not be identified, making use of the table of hydrocarbons shown in Table 10, confirm its retention time by means of test several types of reagents in question.

Table 10. Aromatic hydrocarbon and its density

Name of aromatic hydrocarbon	Symbol	Density (15°C) (g/cm ³)	Number of carbon atoms
Benzene	B	0.884	6
Toluene	To	0.872	7
Ethylbenzene	EB	0.871	8
<i>p</i> -Xylene	pX	0.865	8
<i>m</i> -Xylene	mX	0.868	8
<i>o</i> -Xylene	oX	0.884	8
Isopropylbenzene	iPB	0.866	9
<i>n</i> -Propylbenzene	nPB	0.866	9
1-Methyl-3-ethylbenzene	1M3EB	0.869	9
1-Methyl-4-ethylbenzene	1M4EB	0.865	9
1,3,5-Trimethylbenzene	135TMB	0.869	9
1-Methyl-2-ethylbenzene	1M2EB	0.885	9
1,2,4-Trimethylbenzene	124TMB	0.880	9
1,2,3-Trimethylbenzene	123TMB	0.898	9
Isobutylbenzene	iBB	0.857	10

Table 10. (continued)

Name of aromatic hydrocarbon	Symbol	Density (15°C) (g/cm ³)	Number of carbon atoms
<i>sec</i> -Butylbenzene	secBB	0.866	10
<i>tert</i> -Butylbenzene	tertBB	0.871	10
1-Methyl-3-isopropylbenzene	1M3iPB	0.865	10
1-Methyl-4-isopropylbenzene	1M4iPB	0.861	10
1-Methyl-3-propylbenzene	1M3PB	0.865	10
1,3-Diethylbenzene	13DEB	0.868	10
<i>n</i> -Butylbenzene	nBB	0.864	10
1-Methyl-4-propylbenzene	1M4PB	0.862	10
1-Methyl-2-isopropylbenzene	1M2iPB	0.881	10
1,4-Diethylbenzene	14DEB	0.866	10
1,3-Dimethyl-5-ethylbenzene	13DM5EB	0.869	10
1,2-Diethylbenzene	12DEB	0.884	10
1-Methyl-2-propylbenzene	1M2PB	0.878	10
1,4-Dimethyl-2-ethylbenzene	14DM2EB	0.881	10
1,3-Dimethyl-4-ethylbenzene	13DM4EB	0.880	10
1,2-Dimethyl-4-ethylbenzene	12DM4EB	0.879	10
1,3-Dimethyl-2-ethylbenzene	13DM2EB	0.895	10
1,2-Dimethyl-3-ethylbenzene	12DM3EB	0.896	10
1,2,4,5-Tetramethylbenzene	1245TeMB	0.891	10
1,2,3,5-Tetramethylbenzene	1235TeMB	0.894	10
1,2,3,4-Tetramethylbenzene	1234TeMB	0.909	10
Indane	Indan	0.968	9
Naphthalene	Naph	0.975	10

5.6 Calculation and precision

5.6.1 Calculation Calculation shall be as follows:

- (1) Find the concentration of each aromatic hydrocarbon using the following formula, and calculate to the second decimal place according to the requirements specified in JIS Z 8401.

Round off benzene, toluene, and xylene (total sum of concentrations of *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene) in aromatic hydrocarbons to first decimal place according to the requirements specified in JIS Z 8401.

$$C_{iw} = \frac{A_i \times W_s \times 100}{A_s \times f_{iw} \times W}$$

where, C_{iw} : concentration of aromatic hydrocarbon i (mass%)
 A_i : integrated value of peak area of aromatic hydrocarbon i
 A_s : integrated value of peak area of internal standard material ⁽¹²⁾
 W_s : weighed out amount of internal standard material (g)
 W : weighed out amount of sample (g)
 f_{iw} : mass relative sensitivity relating to number of carbons in aromatic components i ⁽¹³⁾

Notes ⁽¹²⁾ When the sample contains the component whose retention time is the same as that of internal standard material, the integrated value of peak area of the internal standard material shall be obtained according to the following formula.

$$A_s = A - A_b \times \frac{A_c}{A_d}$$

where, A_s : integrated value of peak area of the internal standard material
 A : integrated value of peak area of the sum of the internal standard material (*cis*-decalin or *n*-undecane) and the component which has the same retention time as the internal standard material recorded in 5.5.3.
 A_b : integrated value of peak area of component whose retention time is the same as that of internal standard material recorded in 5.5.2.
 A_c : integrated value of peak area of ethylbenzene recorded in 5.5.3
 A_d : integrated value of peak area of ethylbenzene recorded in 5.5.2

⁽¹³⁾ The mass relative sensitivity obtained in 5.4.3 (2) (c) shall be used for the aromatic hydrocarbon shown in Table 10 whose number of carbons is 8, 9, or 10. In the case of the components in C_8 aromatic hydrocarbon, however, employ the mass relative sensitivity of ethylbenzene, in the case of the components in C_9 aromatic hydrocarbon, that of 1,2,4-trimethylbenzene, and in the case of the components in C_{10} aromatic hydrocarbon, that of *n*-butylbenzene.

Concerning each aromatic hydrocarbon whose identification is impossible, employ the mass relative sensitivity of *n*-butylbenzene.

- (2) Total the concentration of each aromatic hydrocarbon obtained at (1) as shown in the following formula, calculate the concentration of aromatics, and round off to the first decimal place according to JIS Z 8401.

$$C_{AW} = C_{1W} + C_{2W} + C_{3W} + \dots + C_{iW}$$

where, C_{AW} : mass percentage of aromatics (mass%)

C_{iW} : mass percentage of aromatic hydrocarbon i
(mass%)

Remarks: When concentration is expressed with vol%, calculate according to the following formulas. Provided that the density of unidentified aromatic hydrocarbon shall be respectively assumed to be 0.88.

$$C_{iV} = C_{iW} \times \frac{d}{d_i}$$

$$C_{AV} = C_{1V} + C_{2V} + C_{3V} + \dots + C_{iV}$$

where, C_{iV} : volumetric percentage of aromatic hydrocarbon i
(vol%)

C_{AV} : volumetric percentage of aromatics (vol%)

d_i : density of aromatic hydrocarbon shown in Table 10 at 15°C (g/cm³)

d : density of sample at 15°C measured according to the requirements specified in JIS K 2249 (g/cm³)

5.6.2 Precision The tolerance (probability 0.95) on the test results obtained in this test method shall be as follows:

Remarks: If test result falls outside the tolerance, follow the requirements specified in JIS Z 8402.

- (1) Repeatability When test is twice carried out successively in a short time, in the same laboratory, by the same person, using the same apparatus and on the same sample, the allowable difference between test results shall be as shown in Table 11.
- (2) Reproducibility When two tests are carried out in different laboratories, by different persons, using different apparatuses, on the same sample once in each situation, the allowable difference between two test results shall be as shown in Table 11.