

JIS

JAPANESE INDUSTRIAL STANDARD

Fuel gases and natural gas — Methods for chemical analysis and testing

JIS K 2301—1992

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In the event of any doubt arising,
the original Standard in Japanese is to be final authority.

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JAPANESE INDUSTRIAL STANDARD

J I S

Fuel gases and natural gas - Methods for chemical analysis and testing K 2301-1992

1. Scope

This Japanese Industrial Standard specifies methods for chemical analysis of general constituent and special constituent and for testing of calorific value and specific gravity of fuel gases and natural gas. However, this Standard does not apply to liquefied petroleum gas⁽¹⁾ and liquefied natural gas.

Note (¹) The liquefied petroleum gases are in accordance with JIS K 2240.

Remarks 1. Applicable Standards to this Standard are shown in Attached Table 10.

2. Corresponding International Standards are shown in Attached Table 11.

3. Units and numerical values given in { } in this Standard are in accordance with the traditional units and are Standard values.

Further, these traditional units and numerical values become the information reference on and after 1995, 4, 1.

2. Definitions

For the purposes of this Standard, the following definitions apply:

- (1) fuel gas The "fuel gas" means gaseous substances generally used as fuel, such as town gas, coke oven gas, petroleum refinery off gas, oil cracked gas, producer gas, water gas, etc.
- (2) natural gas The "natural gas" means inflammable gas which has methane generated naturally as the principal constituent.
- (3) general constituent The "general constituent" means the principal constituents generally contained in the fuel gas and natural gas, such as methane and other gaseous hydrocarbons, hydrogen, carbon monoxide, carbon dioxide, oxygen, and nitrogen.
- (4) special constituent The "special constituent" means a constituent possibly contained in fuel gas and natural gas, such as total sulphurs, hydrogen sulfide, ammonia, naphthalene, and water content, other than general constituents.

- (5) calorific value The "calorific value" means the calorific value evolved by the complete combustion of gas in air and is expressed by total calorific value per 1 m^3 of dry gas under standard conditions $\text{kJ/m}^3 \{ \text{kcal/m}^3 \}$.
- (6) specific gravity The "specific gravity" means the ratio of the mass of the gas to the mass of dry air of the same volume under the same specific conditions of temperature and pressure near the ordinary temperature and ordinary pressure.
- (7) standard condition The "standard condition" means the condition of gas at a temperature of 0°C under the pressure of 101.32 kPa $\{760 \text{ mmHg}\}$.
- (8) sample gas The "sample gas" means the gas taken out for chemical analysis or testing.

3. Common items

Common items concerning chemical analysis shall, as a rule, be in accordance with the provisions of JIS K 0050, concerning handling of standard reagent, of JIS K 8005, concerning absorptiometry, of JIS K 0115, and concerning gas chromatography, of JIS K 0114.

4. Sampling of gas

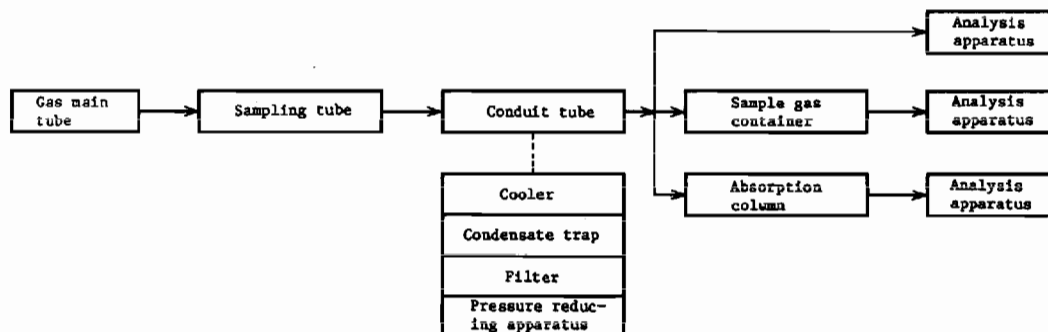
4.1 Sample gas The sample gas shall represent the original gas to be analyzed or tested.

4.2 Sampling position A sample of gas shall be taken from the position of flow where the concentration of constituent is generally even in cross-section and shall avoid the position adjacent to the juncture of the flow.

4.3 Sampling apparatus

4.3.1 The sampling apparatus shall be arranged as shown in Fig. 1 in accordance with the applicable methods for analysis and testing, and be operated in compliance with the procedures specified in the following items according to the condition of the sample gas.

Fig. 1. Example of arrangement of gas sampling apparatus



- (1) A suitable condensate trap shall be provided intermediately in the conduit tube where there is the possibility of moisture in the sample gas being condensated when analyzing the general constituents and measuring the calorific value and specific gravity.
- (2) The sampling tube and conduit tube shall be thermally insulated or heated by suitable means where there is the possibility of moisture or any oily content in the sample gas being condensated and giving the adverse effect to the result of analysis when analyzing the special constituent. If, it is difficult to provide a suitable thermal insulation or heating means and the condensate is separated through the condensate trap in accordance with the procedure specified in (1), the procedure for the analysis of the condensate and the subsequent correction of the analytical results shall be taken.
- (3) If the sample of gas contains tars or dusts, a suitable filter shall be provided intermediately in the sampling tube or conduit tube.
- (4) A suitable cooler shall be provided intermediately in the conduit tube when the sample of gas is taken from a hot source.
- (5) In case the sample of gas is taken from a source under high pressure, a suitable pressure-reducing means shall be provided to prevent moisture or partial constituents from being condensated due to adiabatic expansion when rapidly cooled, and for the purpose of ensuring safe operation.

4.3.2 The material qualities for the sampling tube and conduit tube including cooler, condensate trap, filter, pressure-reducing means which are to be connected as required, and for the several valves and gaskets shall satisfy the following requirements:

- (1) No chemical reaction or adsorption may cause an adverse effect on the analytical and testing results.
- (2) No constituent may cause corrosion.
- (3) Mechanical strength is sufficient for the temperature, pressure, and flow rate of the gas.

4.3.3 The sample gas container and absorption means shall be those specified in paragraphs 4.4 and 6.2 to 6.6.

4.4 Sampling method

4.4.1 General matters General matters for sampling method of sample gas shall be as follows:

- (1) Corresponding to the items for analysis or test, directly take the sample gas or take by introducing the sample gas into absorption apparatus or sample gas container.

- (2) As a preparatory procedure, the sampling tube, conduit tube, cooler, condensate trap, filter, pressure-reducing apparatus, and valves shall be displaced with a sample gas up to just in front of the sampling container and the absorption apparatus.
- (3) The flow rate and volume of the sample gas shall be in accordance with the provisions specified in the respective methods for analysis and testing.
- (4) In the case where the specified flow rate or the volume of sample cannot be obtained due to a lower pressure of the sample gas, a suitable suction pump or booster pump shall be used.
- (5) In the case where the sample gas is taken in a sample gas container, because depending upon the sample gas container the adsorption of gas components into apparatus wall, grease, etc., film permeation, absorption into sealing liquid, etc. are caused, in order to prevent composition change, without allowing to stand for a long time carry out the analysis or test.

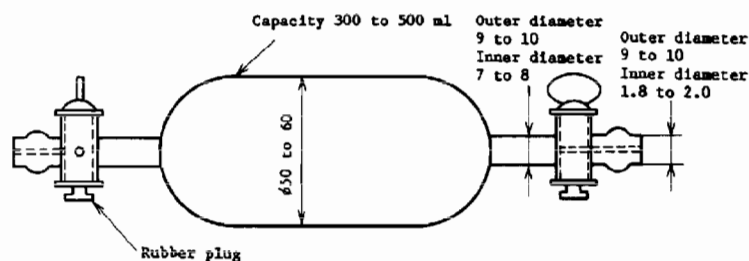
4.4.2 Sampling of gas for analysis of general constituents

The sampling of gas shall be performed according to either of the following methods:

- (1) Introduce the sample gas through sampling tube and conduit tube directly into gas chromatograph.
- (2) Take into the sample gas container. In this case, corresponding to the components of sample gas and condition of sample gas, use either of the following methods.
 - (a) Flowing or vacuum method A sample of gas is taken either by flowing the gas through the sampling bottle as shown in Fig. 2 with a volume at least ten times the capacity of the bottle, or by introducing the gas into the sampling bottle which is preparatorily kept at a vacuum by means of a vacuum pump. A slight amount of water-soluble grease, which does not absorb hydrocarbons, is applied to the cock provided at the sampling bottle.

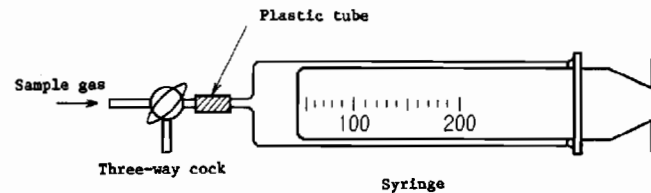
Fig. 2. Gas sampling bottle (An example)

Unit: mm



- (b) Syringe method A sample of gas is taken by introducing into the syringe type sampling apparatus as shown in Fig. 3 by withdrawing the inner cylinder. A slight amount of water-soluble grease as specified in the above (a) shall be applied to the ground root of the syringe.

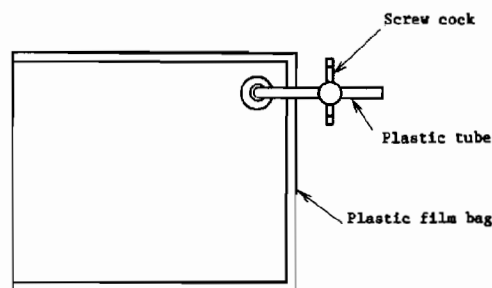
Fig. 3. Syringe type sampling apparatus (An example)



- (c) Gas collecting bag method A sample of gas is taken by introducing the gas into the gas collecting bag with a capacity of 1 l or more as shown in Fig. 4. The gas collecting bag is fabricated of polyester or fluorine resin-based plastic film which does not absorb or adsorb the gaseous constituents and is impermeable thereto⁽²⁾.

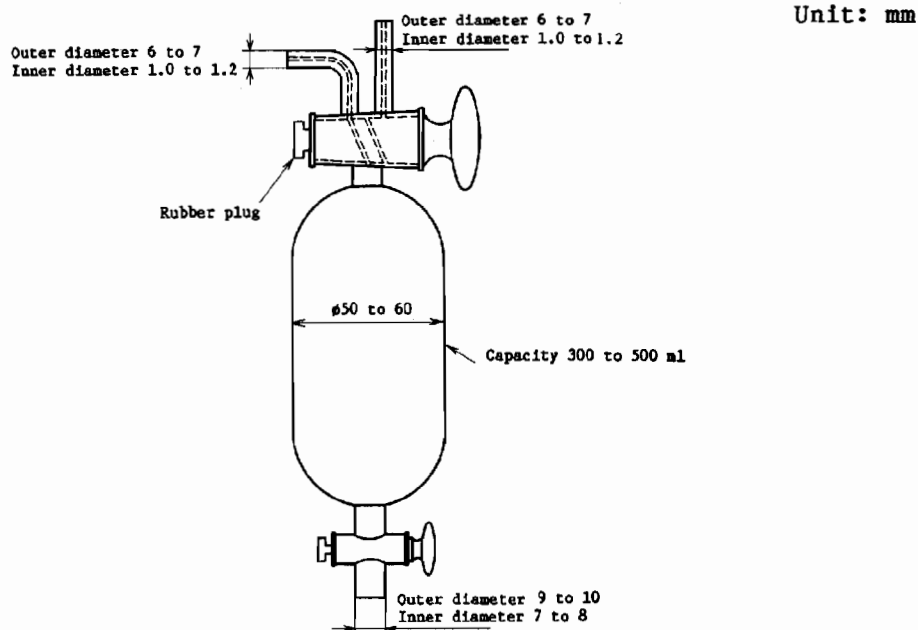
Note ⁽²⁾ This method, in the case where the sample gas must be preserved for a long time, is not applicable.

Fig. 4. Gas collecting bag (An example)



Remarks: According to the sample gas, the sealing liquid displacement method may be used. Fill the sealing liquid into the sampling bottle shown in Fig. 5, and while drawing out the sealing liquid, displace to the sample gas and take out. At this time, make the sealing liquid not to remain in the sampling bottle. As the sealing liquid, dissolve the sodium chloride 220 g specified in JIS K 8150 into water 1 l, make slightly acidic with hydrochloric acid, and after coloring by adding methyl orange indicator (1 g/100 ml) 1 to 2 ml, saturate with the gas of the same composition as that of sample gas to be used. In the case where the acidic gas such as carbon dioxide is contained in the sample gas, because according to the amount the error due to dissolution into the sealing liquid is generated, it should preferably be avoided.

Fig. 5. Gas sampling bottle (An example)



4.4.3 Gas sampling methods for analysis of special constituents One of the following methods shall be selected according to the constituents to be analyzed.

- (1) In the case of analyzing total sulphuric constituents, the sample gas shall be introduced from the conduit tube into the combustion apparatus directly through the gas meter.

In this case, the gas may be collected inside the gas collecting bag with a capacity of 20 to 50 l as shown in Fig. 4, and then the bag shall be installed on the measuring apparatus as shown in Fig. 6 for direct introduction into the combustion apparatus, provided that the gas contains a minimal amount of moisture or oil, and will not condensate itself at ordinary temperature.

- (2) For analysis of hydrogen sulphide, ammonia, and naphthalene, the gas shall, as a rule, be introduced from the conduit tube into the absorption apparatus that is specially specified for each method for analysis.
- (3) For analysis of moisture content, the gas shall be introduced into the moisture absorption apparatus or a dew-point meter through the conduit tube which has a dry interior surface, while taking care to prevent the gas from coming into contact with any moisture or oil. In this case, the conduit tube shall be made of material other than rubber or vinyl. Thick rubber tubing or silicone rubber tubing for vacuum shall be used for connection between the conduit tubes as well as the tube and the absorption apparatus.

4.4.4 Sampling of gas for measurement of calorific value The gas shall be directly introduced into the calorific value measurement apparatus through the conduit tube. Further, in the case where the calorific value is obtained according to calculation from the analysis results of general constituents by gas chromatograph, take out the sample gas according to 4.4.2.

4.4.5 Sampling of gas for measurement of specific gravity The gas shall be directly introduced into the hydrometer or specific gravity measurement apparatus. When the pycnometer method is employed, however, the gas may be collected into the sample gas collecting bag as shown in Fig. 4 and then introduced into the specific gravity measurement apparatus.

Further, in the case of obtaining the specific gravity according to the calculation from the analysis results of general constituents according to gas chromatograph, take out the sample gas according to 4.4.2.

If specific gravity is measured in accordance with the pycnometer method under the wet condition, the sample gas shall be introduced in accordance with the provisions of 4.4.3 (3).

4.5 Volume of sample gas The volume of the sample gas taken shall be measured by wet type gas meter, and at the same time shall be converted into the volume of dry gas at standard conditions by reading out atmospheric pressure, gas temperature, and gas pressure according to the following formula:

$$V_0 = V_1 \times \frac{273.15}{t_g + 273.15} \times \frac{1}{P_0} \times (B_0 + P - S) \times f_2$$

where, V_0 : volume of dry sample gas at standard conditions (l)

V_1 : volume of sample gas at the time of measurement (l)

t_g : temperature of sample gas at the time of measurement (°C)

P_0 : standard atmospheric pressure (101.32 kPa){760 mmHg}

B_0 : atmospheric pressure (kPa){ mmHg } at 0°C, and obtained according to the following formula.

$$B_0 = B - \alpha$$

where, B : indicated value by barometer (kPa){mmHg}

α : correcting value for conversion into atmospheric pressure, to be obtained from Attached Table 1 or 2 (kPa){mmHg}

P : gas pressure at gas meter (kPa){mmHg}.

In the case where the gas pressure is measured by (mmH₂O), if its value is taken as P_w , P is converted according to the following formula.

$$P = \frac{9.8}{1000} P_w (\text{kPa}) \text{ [or } P = \frac{1}{13.6} P_w (\text{mmHg})]$$

S : pressure of saturated water vapor at t_g (kPa){mmHg} to be determined according to Attached Table 3 or 4.

f_2 : gas meter correction coefficient

Meanwhile, it is preferable to use Attached Table 5 or 6 to obtain the value $\frac{273.15}{t_g + 273.15} \times \frac{1}{P_0}$ in the formula.

Remarks: In the case where total sulphuric constituents are to be analyzed, the volume of the sample gas may be measured by a gas meter for the gas collecting bag.

An example of such gas meter is shown in Fig. 6. Operation and calculation of the volume of the sample gas shall be carried out in accordance with the following procedures:

(1) Operation

- (a) Open cock ①, and start up the pump ① to supply water into the metal measuring tank with a gauge.
- (b) Open cock ②, and start up the pump ② to transfer half the water in the metal water tank with internal marked line into the water storage tank.
- (c) Submerge the gas-collecting bag filled with the sample gas into the metal water tank with internal marked line, and hold the bag down with a keep plate.
- (d) Open cock ③, and start up the pump ③ to supply water into the water storage tank up to the level of water-mark line, while taking care to prevent formation of air bubbles between the gas collecting bag and the keep plate.
- (e) Open cock ⑤, and burn off a predetermined quantity of the sample gas in accordance with 6.2.1 (3). After burning is completed, open the cock ④ and fill the measuring water tank with water up to the level of the marked line.

- (2) Volume of sample gas Obtain the volume of sample gas at standard conditions from the reading of the scale of the measuring water tank according to the following formula:

$$V_0 = V_1 \times \frac{273.15}{t_g + 273.15} \times \frac{1}{P_0} \times (B_0 + P)$$

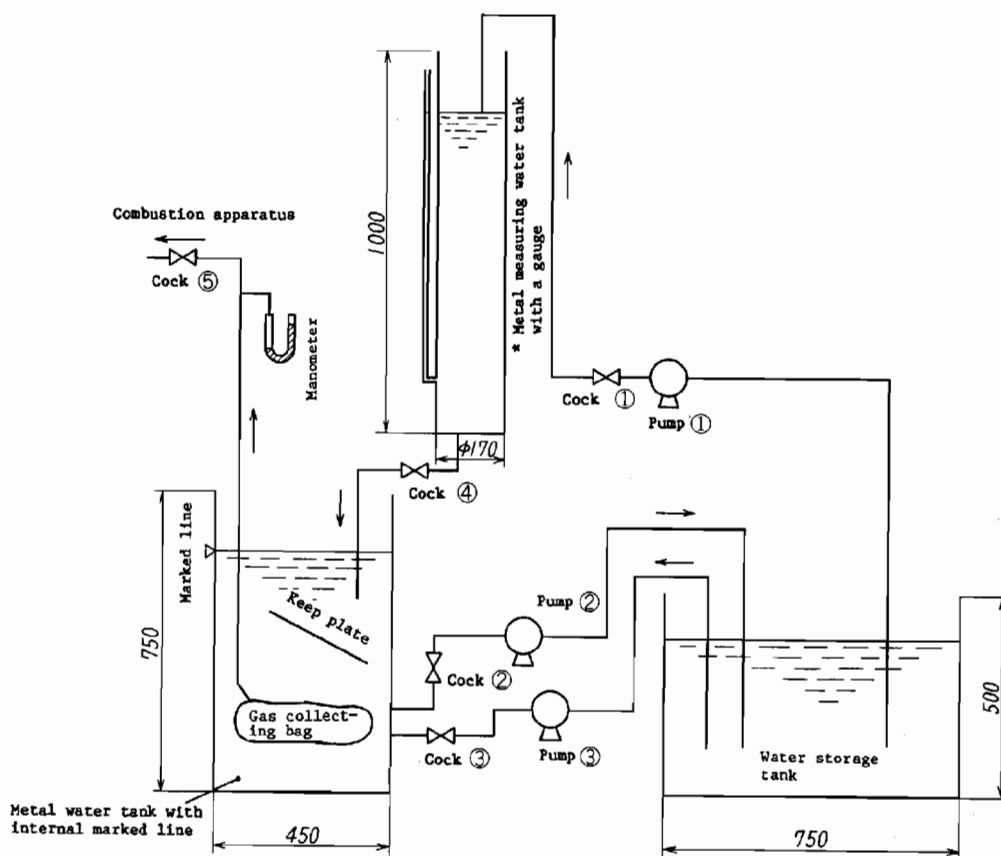
where, V_1 : volume of sample gas at the time of measurement (l)
(quantity of water reduced in the metal measuring water tank with a gauge)

t_g : temperature of sample gas at the time of measurement (°C)
(water temperature in the metal water tank with internal marked line)

P : pressure inside the gas collecting bag (kPa){ mmHg }
(mercury column converted from the water column in a manometer)

Fig. 6. Gas measuring apparatus for gas collecting bag (An example)

Unit: mm



Note *: This is graduated every 1 cm, and preparatorily checked that 1 cm is equivalent to how many ml.

5. Methods for analysis of general constituents (Gas chromatography)

5.1 Summary This method is a means of separating each of the constituents in the sample gas through a combination of several types of columns by the use of a gas chromatograph that comprises a thermal conductivity type detector or hydrogen flame ionization detector and by subsequently comparing the peak area given on the chromatogram with the peak area of the mixed standard gas or pure gas under the same conditions, and thereby determining the content of each constituent after being corrected by a correction coefficient.

5.2 Constituents to be analyzed The analysis objective constituents of this method shall be as follows:

Hydrogen (H_2)	Isobutane ($i-C_4H_{10}$)
Oxygen (O_2)	Butane ($n-C_4H_{10}$)
Nitrogen (N_2)	Butene-series (C_4H_8)
Carbon Monoxide (CO)	1,3-butadiene (C_4H_6)
Carbon dioxide (CO_2)	Isopentane ($i-C_5H_{12}$)
Methane (CH_4)	Pentene ($n-C_5H_{12}$)
Ethane (C_2H_6)	Neopentane ($neo-C_5H_{12}$)
Ethylene (C_2H_4)	Pentene-series (C_5H_{10})
Propane (C_3H_8)	Cyclopentane ($cyclo-C_5H_{10}$)
Propylene (C_3H_6)	Hexane series (C_6H_{14})
	Benzene (C_6H_6)
	Toluene ($C_6H_5CH_3$)

Remarks 1. The butene-series shall include 1-butene, cis-2-butene, trans-2-butene, isobutene; the pentene-series shall include 1-pentene, cis-2-pentene, trans-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene; and the hexane-series shall include hexane, isohexane, 3-methyl-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane. However, as for natural gas, the hexane-series may include cyclopentane.

Further, the butene-series, pentene-series, and hexane-series indicate the results of quantitative analysis for each constituent, as a rule.

- When it is obvious that the sample gas is taken from the natural gas or petroleum gas, and does not contain any constituent such as hydrogen, carbon monoxide, or ethylene, such kind of constituents need not to be analyzed.
- As to the hydrocarbon series not less than C_6 which may be included in natural gas and the like, the constituents not less than C_6 are measured quantitatively in integration by applying back flushing and indicated as C_6+ .

5.3 Apparatus

5.3.1 Gas chromatograph⁽³⁾ The main components of the gas chromatograph shall satisfy the following requirements:

Note ⁽³⁾ The gas chromatograph, in order to avoid complexity such as column exchange, exchange of analysis conditions and to shorten the analysis time, plural stands for each column should preferably be set or plural flow route type gas chromatograph, be utilized.

(1) Detector

- (a) Thermal conductivity detector The thermal conductivity detector having the capability of obtaining about 1500 in S value (mV) by calculation according to the following formula, when the column (d), (e) or (f) shown in Table 1 are connected to the gas chromatograph and propane is introduced with helium as the carrier gas under the analytical conditions of Table 2.

In the case where the peak area is measured by data processor, obtain according to the following formula.

$$S = \frac{C \times F \times 10^{-3}}{60 \times Q}$$

where, C : peak area of propane by data processor ($\mu\text{V}\cdot\text{s}$)

F : flow rate of carrier gas (ml/min)

Q : quantity of propane introduced (ml)

In the case where the peak area is measured by peak width at half-height method, obtain according to the following formula.

$$S = \frac{D \times F \times A}{V \times Q}$$

where, D : recorder sensitivity per graduation width 1 cm on the record chart (mV/cm)

F : flow rate of carrier gas (ml/min)

A : peak area of propane by the peak width at half-height method (cm^2)

V : feed speed of record chart (cm/min)

Q : quantity of propane introduced (ml)

- (b) Hydrogen flame ionization detector The hydrogen flame ionization detector having the capability of obtaining about 0.001 in ρ value (coulomb/g) by calculation according to the following formula, when the column (g) shown in Table 1 is connected to the gas chromatograph and benzene specified in JIS K 8858 is introduced with nitrogen as the carrier gas under the analytical conditions of Table 2.

In the case where the peak area is measured by a data processor, obtain according to the following formula.

$$\rho = \frac{C \times 10^{-6}}{R \times W}$$

where, C : peak area of benzene by data processor ($\mu\text{V}\cdot\text{s}$)

W : amount of benzene introduced (g)

R : dynamic range of gas chromatograph (□)

In the case where the peak area is measured by peak width at half-height method, obtain according to the following formula.

$$\rho = \frac{D \times A \times 60 \times 10^{-3}}{V \times R \times W}$$

where, D : recorder sensitivity per graduation width 1 cm on the record chart (mV/cm)

V : feed speed of record chart (cm/min)

R : dynamic range of gas chromatograph (Ω)

A : peak area of benzene by the peak width at half-height method (cm²)

W : quantity of benzene introduced (g)

- (2) Sensitivity-change-over apparatus The sensitivity-change-over apparatus shall have a maximum attenuation ratio of not less than 500:1 and the attenuator accuracy, within 0.5 % at each step.
- (3) Column tank The column tank shall be capable of containing the column specified in 5.5, and be capable of maintaining the set temperature within a range of stability of $\pm 0.3^{\circ}\text{C}$.

Remarks: In the case of performing analysis by raising temperature, preliminarily confirm that the reproducibility of raising temperature programme is sufficient.

- (4) Flow rate control mechanism The flow rate adjusting valve for the carrier gas shall be capable of controlling stability the pressure within 1 % of the set pressure.

5.3.2 Gaseous sample introduction apparatus The gaseous sample introduction apparatus shall be designed to receive a sample gas measuring tube of 0.1 to 5 ml capacity, and be capable of satisfying the repeatability specified in 5.7 (3).

Proper selection shall be made for the volume of the sample gas measuring tube according to the concentration of the constituents to be analyzed and to the sensitivity of the detector.

5.3.3 Recorder The recorder shall be capable of the following performances, excepting where data processor specified in 5.3.4 is used.

- (1) Full scale 1 mV
- (2) Valid width of record chart 20 cm or more
- (3) Running time of pen 1 s or less per 99 % of full scale
- (4) Chart speed To be adjustable by 0.5 cm/min or more, as necessary.
- (5) Dead zone Within 0.15 % of full scale

5.3.4 Data processor A data processor is used to indicate the signal corresponding to the peak area of the constituent shown on the gas chromatogram in numerical value, and shall have the following performances:

- (1) Integrating sensitivity 1 count or more per 1 $\mu\text{V}\cdot\text{s}$
- (2) Accuracy Coefficient of variation for the ratio of peak area of nitrogen to that of oxygen (N_2/O_2) is within $\pm 0.5\%$ when the data processor is connected to the gas chromatograph and the air is repeatedly analyzed three times or more under the analysis conditions shown in Table 2.
- (3) Linearity Within $\pm 0.1\%$ to a measured input of 1 mV or more
- (4) Input voltage 1000 mV max.

5.4 Carrier gas, hydrogen gas, and ignition improving gas The carrier gas, hydrogen gas and ignition improving gas shall be as follows:

- (1) Carrier gas Use the helium and nitrogen having purity of 99.9 vol % or more. Instead of helium or nitrogen argon (purity of 99.9 vol % or more) may be used.
- (2) Hydrogen gas As to fuel gas of hydrogen flame ionization detector, use the hydrogen equivalent or superior to grade 4 (purity of 99.9 vol % or more) specified in JIS K 0512.
- (3) Ignition improving gas As to ignition improving gas of hydrogen flame ionization detector, use the air or oxygen demineralized, refined of 0.196 MPa{2 kgf/cm²} or more in pressure.

5.5 Column The column shall be in accordance with the following:

- (1) Tube The tube used for the column is made of copper, stainless steel, glass, etc., with the internal diameter and length as shown in Table 1, and has end fittings firmly securable with the gas chromatograph.
- (2) Column packing materials Packing materials for the column shall have necessary, sufficient separating characteristics for the constituents being analyzed, as cited, for example, in Table 1.

Table 1. Example of columns

Type of column		Packing material for column (An example)			Tube	
		Stationary-phase liquid	Type of carrier	Grain diameter of carrier μm	I.D. mm	Length m
a	Synthetic zeolite	Synthetic zeolite 13X-type (Na salt), or 5A-type (Ca salt)		177 to 250	3 to 5	1.5 to 3
b	Polymer beads	Porous polymer beads				2 to 4
c	Silica gel	Silica gel				1 to 2
d	Sebaco nitrile	Sebaco nitrile 25 %	Brown diatomaceous earth			8 to 10
e	n PS-DMS	n -propyl sulfone-dimethylsulfolane (75:25) mixed solution 35 %	Brown diatomaceous earth	250 to 590	4 to 5	13 to 15
f	DOP	Diocetyl phthalate 25 %	Brown diatomaceous earth	177 to 250	3 to 5	5 to 7
g	PEG6000	Polyethylene glycol 25 %	Brown diatomaceous earth			1.5 to 3
h	Melt silica capillary	$\text{Al}_2\text{O}_3/\text{kCl}$			0.3	50

Informative reference: As to synthetic zeolite, there are molecular seave 13X, molecular seave 5A on the market.

Further for polymer beads, these is polapack Q on the market.

- (3) Packing method Using glass cotton, lightly plug up one end of the tube of which the internal surface has been thoroughly washed and dried, and then let each small amount of packing material flow from the other end of tube while vibrating the tube or sucking until the tube is evenly and consistently packed with no voids remaining. Finally plug up the other end lightly with glass cotton.
- (4) Prior heating of column Connect the column to the gas chromatograph at a predetermined position, and heat up the column while flowing the carrier gas and adjusting the temperature of the column tank so that it rises higher than the working temperature (but not higher than the maximum using temperature) until the remaining solvents and the like, are removed. In this case, one end of the detector's side of column is not be connected to the detector.

- (5) **Combination of column** It is necessary to use several type columns in combination for analysis of all compositions.

Examples of combinations of columns and analytical conditions are shown in Table 2, but if the separating elution of all constituents of sample gas is confirmed, it may be analyzed under other column combination and analysis conditions.

Table 2. Examples of combination of columns and analytical conditions

Combination of columns	Type of column	Constituents to be analysed	Analytical conditions			Type of standard gas	
			Tank temperature °C	Carrier gas	Flow rate ml/min	Pure gas	Mixed standard gas
A	Synthetic zeolite	H ₂	Ordinary temperature to 70	N ₂	30 to 60	H ₂	Use 5.6 (1),
	Synthetic zeolite	O ₂ , N ₂ , CH ₄ , CO	Ordinary temperature to 70	He		N ₂ or CH ₄	
	WPS-DMS	C ₂ H ₄ , C ₂ H ₆ , CO ₂ , C ₃ to C ₅ constituents	Ordinary temperature to 40	He		C ₃ H ₈	
	PEG6000	C ₆ H ₆ , C ₆ H ₅ CH ₃	80 to 120	He		-	
B	Synthetic zeolite	H ₂	Ordinary temperature to 70	N ₂	30 to 60	H ₂	
	Synthetic zeolite	O ₂ , N ₂ , CH ₄ , CO	Ordinary temperature to 70	He		N ₂ or CH ₄	
	Polymer beads	C ₂ H ₄ , C ₂ H ₆ , CO ₂	50 to 100	He		CO ₂	
	Sebacol nitrile	C ₃ to C ₆ constituents	Ordinary temperature to 60	He		C ₃ H ₈	
C	Synthetic zeolite	O ₂ , N ₂ , CH ₄	Ordinary temperature to 70	He	30 to 60	CH ₄	
	Silica gel	C ₂ H ₆ , CO ₂	50 to 70	He		CO ₂	
	DOP	C ₃ to C ₆ constituents	50 to 70	He		C ₃ H ₈	
D	Synthetic zeolite	H ₂	Ordinary temperature to 70	N ₂	30 to 60	H ₂	
	Synthetic zeolite	O ₂ , N ₂ , CH ₄ , CO	Ordinary temperature to 70	He		N ₂ or CH ₄	
	Polymer beads	C ₂ H ₄ , C ₂ H ₆ , CO ₂	50 to 100	He		CO ₂	
	Melt silica capillary	C ₃ to C ₆ constituents, C ₆ H ₆ , C ₆ H ₅ CH ₃	100 → 200 raising temperature	He	2 to 3	C ₃ H ₈	

5.6 **Standard gas** The standard gas to be referred to in the analysis of the sample gas shall be as follows.

- (1) **Mixed standard gas** Use the mixed gas of known concentration resembling the composition of sample gas.

Remarks 1. The mixed standard gas should preferably be contained with all constituents contained in sample gas to be analyzed, but relating to the constituent which is difficult to be filled in the high pressure container integrally such as oxygen, a certain type non-saturated hydrocarbon, high boiling point hydrocarbon, etc., use it by dividing into plural mixed standard gas. In case where even in this method it is not suitable, omit the containing, and calculate the omitted constituent by using the peak area value of other constituent contained in mixed standard gas, correction factor and concentration (Refer to 5.8).

2. The mixed standard gas of benzene or toluene difficult in filling in high-pressure container may be prepared according to the method specified in JIS K 0088, as appropriate.

(2) Pure gas Examples of pure gas to be used for analysis of sample gas are shown in the following:

Hydrogen Hydrogen of grade 3 specified in JIS K 0512 or more (purity 99.99 vol % or more)

Nitrogen Nitrogen of grade 2 specified in JIS K 1107 or more (purity 99.99 vol % or more)

Methane Purity 99.9 vol % or more

Carbon dioxide Purity 99.9 vol % or more

Propane Purity 99.5 vol % or more

Butane Purity 99.5 vol % or more

Remarks: The method to use the pure gas is easy in obtaining pure gas and is a simple, convenient method, but the correction factor may vary due to the apparatus, analysis conditions, etc., and therefore in order to perform analysis with accuracy the actually measured value should preferably be used for each gas chromatograph to be used.

5.7 Operation The operation shall be carried out according to the following procedures:

(1) Adjustment of gas chromatograph Prior to analysis, preliminarily adjust the gas chromatograph.

Informative reference: To be in accordance with handling manual of respective using apparatuses.

(2) Stabilization of gas chromatograph After setting the sensitivity exchange apparatus at the measuring conditions, start the recorder, and stabilize the gas chromatograph until the drift of base line becomes 1 % or less of recorder full scale in 10 min.

- (3) Confirmation of gas chromatograph for stability Introduce the standard gas into the sample gas measuring tube, alter the passage of the sample gas introduction apparatus to introduce the sample gas into the column so that the chromatogram can be recorded on the chart⁽⁴⁾. Repeat this procedure two times, and confirm that relating to the largest peak the difference in the peak height or in the count of the data processor between these two operations is within 1 % of the height or count⁽⁵⁾.

Notes (4) Alter the sensitivity change-over apparatus appropriately to ensure that the peak of constituent may be as high as possible within the range of maximum movement of the pen, excepting where the data processor is used.

(5) If the difference is more than 1 %, suspect an imperfect displacement in the sample gas measuring tube, leakage of sample introduction apparatus, or an improperly operated sample gas introducing operation. These shall then be checked.

- (4) Introduction of standard gas Introduce the standard gas⁽⁶⁾ by using the same procedure as in (3), and record the chromatogram⁽⁴⁾.

Note (6) This operation may be made common with that defined in (3), but it is preferable to take this operation at least once at starting of analysis of one day or the analysis conditions are changed.

- (5) Introduction of sample gas After the sample gas container or conduit tube has been connected to the sample introduction apparatus, the sample gas has been flowed to the sample gas measuring tube and displacement has been achieved, alter the sample introduction passage to introduce the sample gas into the column, and then record the chromatogram on the chart⁽⁴⁾.
- (6) Identification of constituents The chromatogram obtained in (5) shall be submitted to identify the respective constituents at each peak by comparing with the sample of known constituent to know the retaining time, or with reference to Figs. 8 to 17.
- (7) Measurement of peak area The peak areas appearing in the chromatogram of the standard gas and of each analytical constituent to be analyzed are measured by the peak width at half height method or by data processor method. If it is analyzed by a capillary column, measure the peak area by the data processor method.
- (a) Data processor using method Take the count indicated by data processor as the peak area integral value.

- (b) Peak width at half-height method As shown in Fig. 7, the peak of chromatogram obtained is precisely measured by means of the gauge with an auxiliary rule up to 0.5 mm for height of peak and 0.1 mm for peak width at half height. The peak area (A) is calculated according to the following formula:

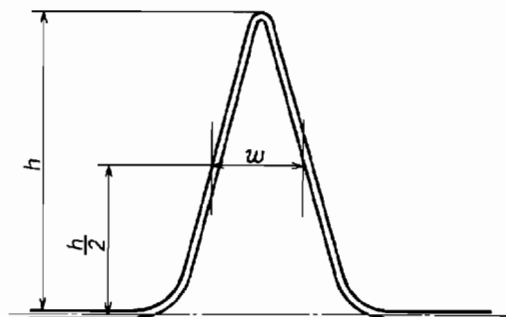
$$A = w \times h \times R (\text{mm}^2)$$

where, w : peak width at half height (mm)

h : height of peak (mm)

R : attenuation ratio of the sensitivity-change-over apparatus.

Fig. 7. Measuring method for peak area by peak width at half height method (In the case of symmetrical peak)



5.8 Calculation Calculation shall be made according to the following procedures:

- (1) Calculate the concentration of each constituent according to the following formula:

(1.1) In the case of using mixed standard gas

- (a) In the case of calculating constituent contained in mixed standard gas

$$C'_{vi} = \frac{A_i \times P_i}{A_s}$$

where, C'_{vi} : calculating concentration of constituent i in sample gas (vol %)

A_i : peak area of constituent i in sample gas (mm² or count)

A_s : peak area of constituent i in mixed standard gas (mm² or count)

P_i : concentration of constituent i in mixed standard gas (vol %)

- (b) In the case of calculating constituent not contained in mixed standard gas

$$C'_{vi} = \frac{A_i \times f_i \times C_{vs}}{A_s}$$

where, C'_{vi} : calculating concentration of constituent i in sample gas (vol %)

C_{vs} : concentration of constituent to be reference in mixed standard gas (vol %)

A_i : peak area of constituent i in sample gas (mm² or count)

A_s : peak area of constituent to be reference in mixed standard gas (mm² or count)

f_i : correction factor of constituent i to be constituent to be reference

However, because the correction factor (f_i) of constituent i may vary more or less due to apparatus and conditions, as a rule, the actually measured value is used. In the case free from interference specially, the correction factor of Table 3 or Table 4 may be used.

- (1.2) In the case of using pure gas

- (a) In the case of direct calculating of pure gas constituent

$$C'_{vi} = \frac{A_i \times P}{A_s}$$

where, C'_{vi} : calculating concentration of constituent i in sample gas (vol %)

A_i : peak area of constituent i in sample gas (mm² or count)

A_s : peak area of pure gas (mm² or count)

P : purity of pure gas (vol %)

- (b) In the case of calculating of constituent other than pure gas constituent

$$C'_{vi} = \frac{A_i \times f_i \times P}{A_s}$$

where, C'_{vi} : calculating concentration of constituent i in sample gas

A_i : peak area of constituent i in sample gas (mm² or count)

A_s : peak area of pure gas (mm² or count)

f_i : correction factor of constituent i to reference constituent

P : purity of pure gas (vol %)

However, because the correction factor (f_i) of constituent i may vary more or less due to apparatus and conditions, as a rule, the actually measured value is used. In the case free from interference specially, the correction factor of Table 3 or Table 4 may be used.

Remarks: According to Remarks 3 to 5.2, in the case where the high-boiling point hydrocarbon not less than C_6 is determined as C_6^+ integrally by using back flushing operation, when the paraffine series are the main constituents, calculate with estimating as hexane and when the aromatic hydrocarbon series are main constituents, calculate with estimating as benzene.

- (2) Obtain the aggregated value of the calculating concentration of each constituent in (1), and when the value is within the range of 98.00 through 102.00 vol % ⁽⁷⁾, the analytical value for each constituent shall be calculated according to the following formula:

$$C_{vi} = \frac{C'_{vi}}{\Sigma C'_{vi}} \times 100$$

where, C_{vi} : analytical value of the constituent i in the sample gas (vol %)

C'_{vi} : calculating concentration of the constituent i in the sample gas (vol %)

$\Sigma C'_{vi}$: aggregated value of the calculating concentration of each constituent (vol %)

Note (7) If the aggregated value of the calculating concentration of each constituent deviates from the range of 98.00 through 102.00 vol %, suspect serious error in the adjustment of the apparatus, in the analytical operation, or in calculation, or the inclusion of constituents other than those being analyzed. A thorough check shall then be made.

Table 3. Correction factor for constituents in thermal conductivity type gas chromatograph (f_i)

Carrier gas			Nitrogen	Helium				
Constituent to be analyzed	Standard gas			Hydrogen	Nitrogen	Methane	Carbon dioxide	Propane
	1	Hydrogen	H ₂	1.00				
2	Oxygen	O ₂		1.05	0.90			
3	Nitrogen	N ₂		1.00	0.86			
4	Carbon monoxide	CO		1.00	0.86			
5	Carbon dioxide	CO ₂		0.88	0.75	1.00	1.35	
6	Methane	CH ₄		1.17	1.00		1.80	
7	Ethane	C ₂ H ₆				0.94	1.27	
8	Ethylene	C ₂ H ₄				1.00	1.35	
9	Propane	C ₃ H ₈				0.74	1.00	
10	Propylene	C ₃ H ₆				0.76	1.03	
11	Isobutane	<i>i</i> -C ₄ H ₁₀					0.79	1.04
12	Butane	<i>n</i> -C ₄ H ₁₀					0.76	1.00
13	1-Butene	1-C ₄ H ₈					0.80	1.05
14	Trans-2-butene	<i>trans</i> -2-C ₄ H ₈					0.76	1.00
15	Cis-2-butene	<i>cis</i> -2-C ₄ H ₈					0.75	0.99
16	Iso-butene ⁽⁸⁾	<i>i</i> -C ₄ H ₈					0.79	1.04
17	1,3-Butadiene	1, 3-C ₄ H ₆					0.81	1.07
18	Iso-pentane ⁽⁸⁾	<i>i</i> -C ₅ H ₁₂					0.65	0.86
19	Pentane	<i>n</i> -C ₅ H ₁₂					0.62	0.82
20	1-Pentene ⁽⁸⁾	1-C ₅ H ₁₀					0.63	0.83
21	Cyclopentane	<i>cyclo</i> -C ₅ H ₁₀					0.67	0.88
22	Iso-hexane	<i>i</i> -C ₆ H ₁₄					0.54	0.71
23	Hexane ⁽⁸⁾	<i>n</i> -C ₆ H ₁₄					0.53	0.70
24	Benzene	C ₆ H ₆					0.65	0.86
25	Toluene	C ₆ H ₅ CH ₃					0.56	0.74

Note (8) Iso-butene may represent butene-series; iso-pentane may represent neopentane; 1-pentene may represent pentene-series; hexane may represent hexane-series.

Table 4. Constituent correction factor in hydrogen flame ionization type gas chromatograph (f_i)

Carrier gas			Nitrogen	
Constituent to be analyzed	Standard gas			
		Butane	Propane	
1 Methane	CH ₄		3.2	
2 Ethane	C ₂ H ₆		1.5	
3 Ethylene	C ₂ H ₄		1.5	
4 Propane	C ₃ H ₈		1.0	
5 Propylene	C ₃ H ₆		1.05	
6 Iso-butane	<i>i</i> -C ₄ H ₁₀	1.0	0.75	
7 Butane	<i>n</i> -C ₄ H ₁₀	1.0	0.75	
8 1-Butene	1-C ₄ H ₈	1.0	0.75	
9 Trans-2-butene	<i>trans</i> -2-C ₄ H ₈	1.0	0.75	
10 Cis-2-butene	<i>cis</i> -2-C ₄ H ₈	1.0	0.75	
11 Iso-butene(⁹)	<i>i</i> -C ₄ H ₈	1.0	0.75	
12 1,3-Butadiene	1,3-C ₄ H ₆	1.0	0.75	
13 Iso-pentane(⁹)	<i>i</i> -C ₅ H ₁₂	0.77	0.58	
14 Pentane	<i>n</i> -C ₅ H ₁₂	0.77	0.58	
15 1-Pentene(⁹)	1-C ₅ H ₁₀	0.77	0.58	
16 Cyclopentane	<i>cyclo</i> -C ₅ H ₁₀	0.80	0.60	
17 Iso-hexane	<i>i</i> -C ₆ H ₁₄	0.63	0.47	
18 Hexane(⁹)	<i>n</i> -C ₆ H ₁₄	0.63	0.47	
19 Benzene	C ₆ H ₆	0.69	0.52	
20 Toluene	C ₆ H ₅ CH ₃	0.61	0.45	

Note ⁽⁹⁾ Iso-butene may represent butene-series; iso-pentane may represent neopentane; 1-pentene may represent pentene-series; hexane may represent hexane-series.

5.9 Expression of analysis results

- (1) The analysis values of respective constituents shall be expressed by rounding off to two places of decimals according to JIS Z 8401. If the aggregate does not become 100.00 vol %, increase or decrease the largest numerical value out of the constituent analysis values and make the aggregate coincident with 100.00 vol %.
- (2) The tolerance of analysis values when carried out twice successively by the same person by using the same apparatus on the same sample shall be as shown in Table 5⁽¹⁰⁾.

Note (¹⁰) In case where it is difficult to carry out the analysis twice on the same sample, by using the mixed standard gas resembling composition as that of sample gas, the confirming of accuracy may be carried out preliminarily.

Table 5. Tolerances for gas chromatograph analysis method

		Unit: vol%
Analysis value		Tolerance
Less than 1		0.03
1 min.	less than 5	0.05
5 min.	less than 25	0.15
25 min.		0.30

Fig. 8. Chromatogram on synthetic zeolite
 (Example 1) (Determination of hydrogen)

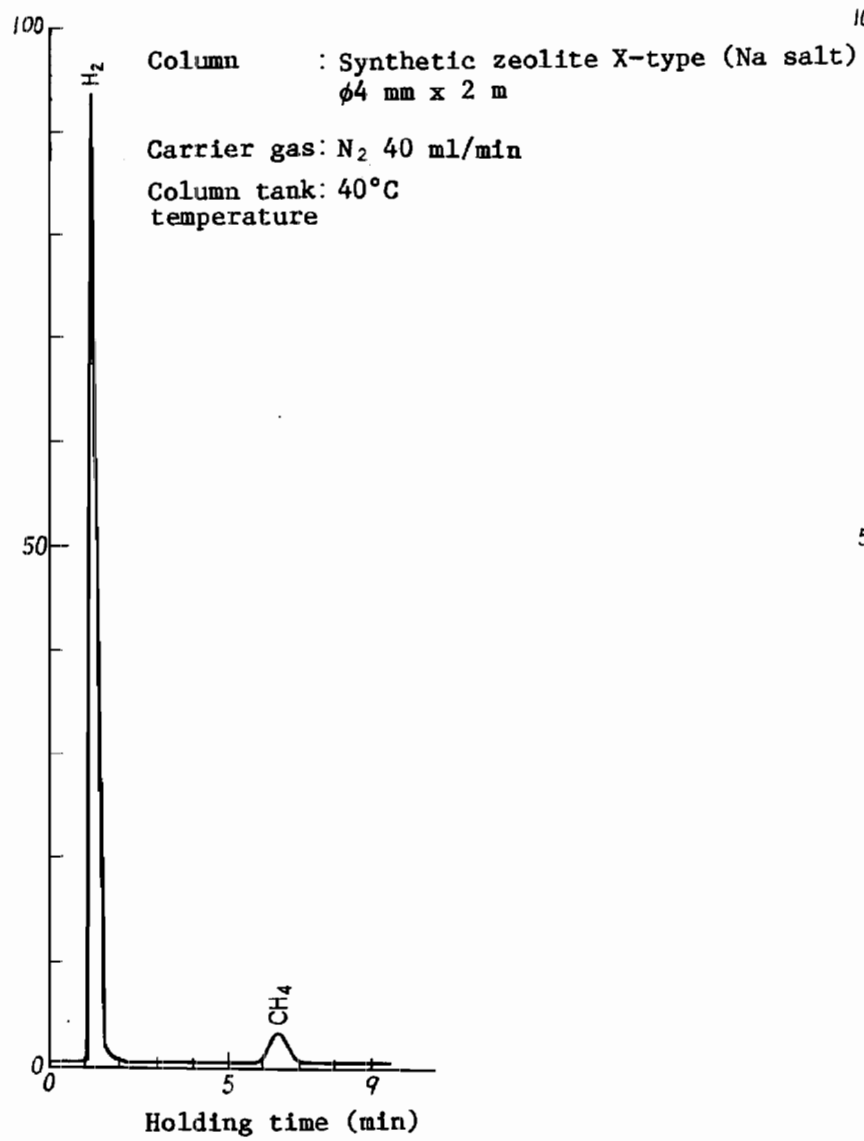
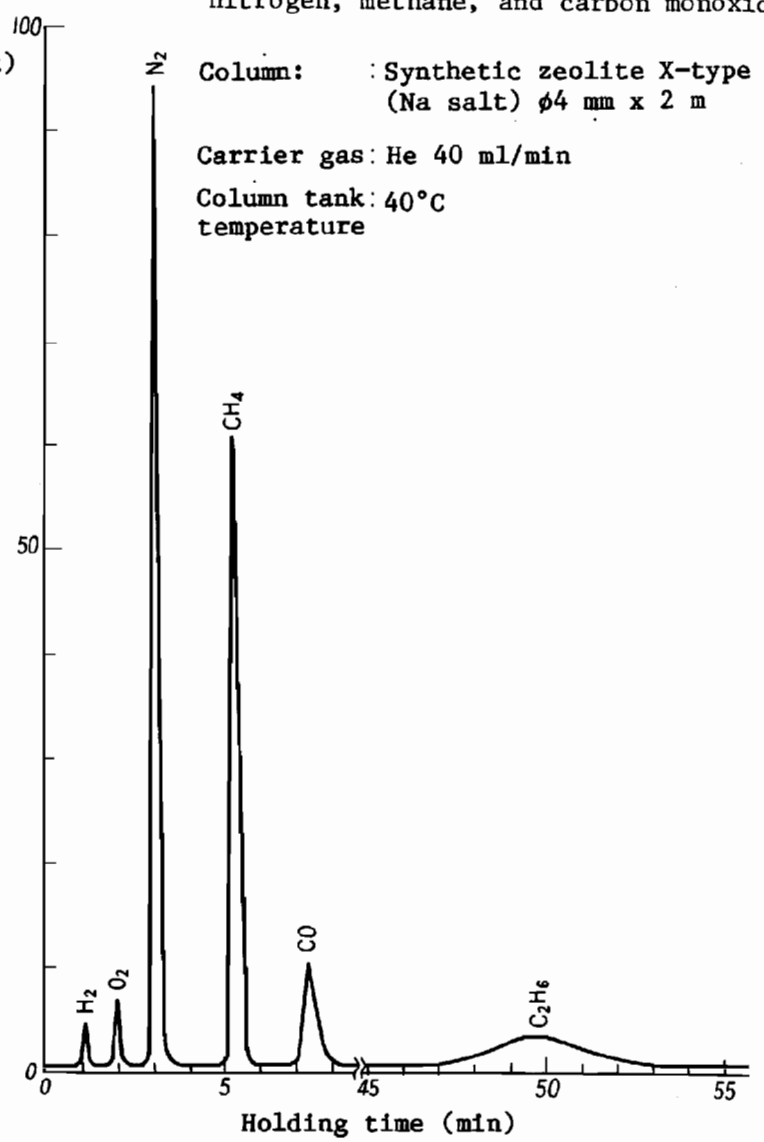


Fig. 9. Chromatogram on synthetic zeolite
 (Example 2) (Determination of oxygen,
 nitrogen, methane, and carbon monoxide)



K 2301-1992²⁴

JIS K 2301 92 ■ 4933608 0504769 200 ■

Fig. 10. Chromatogram on polymer beads (Example)

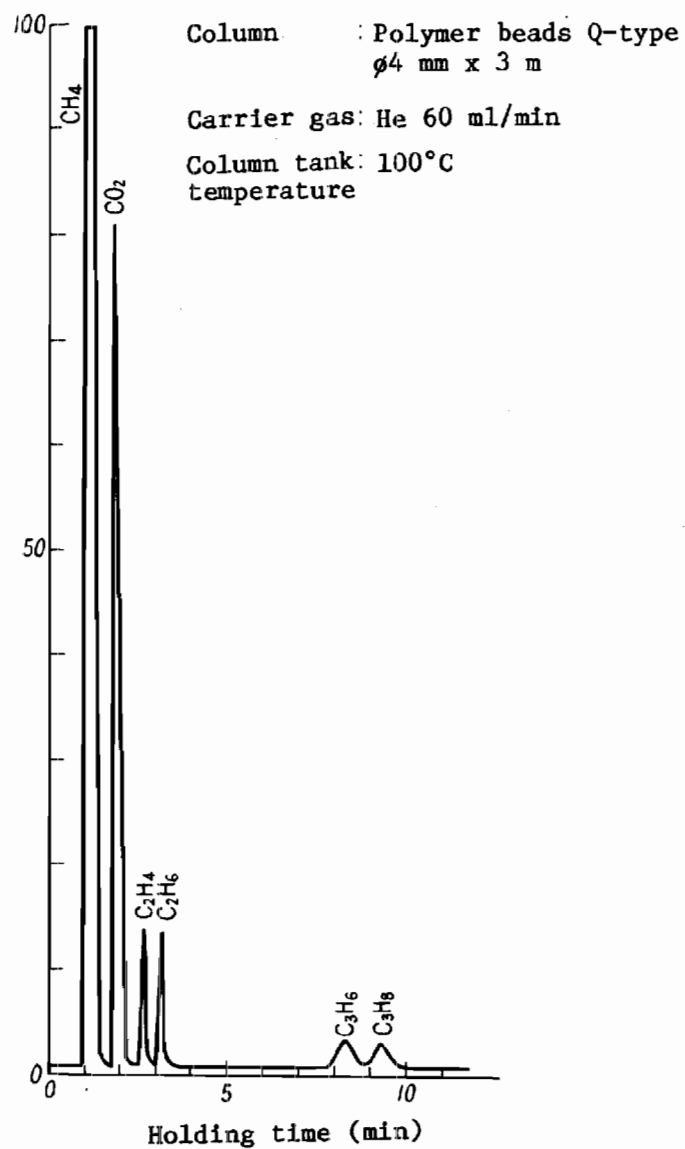


Fig. 11. Chromatogram on silica gel (Example)

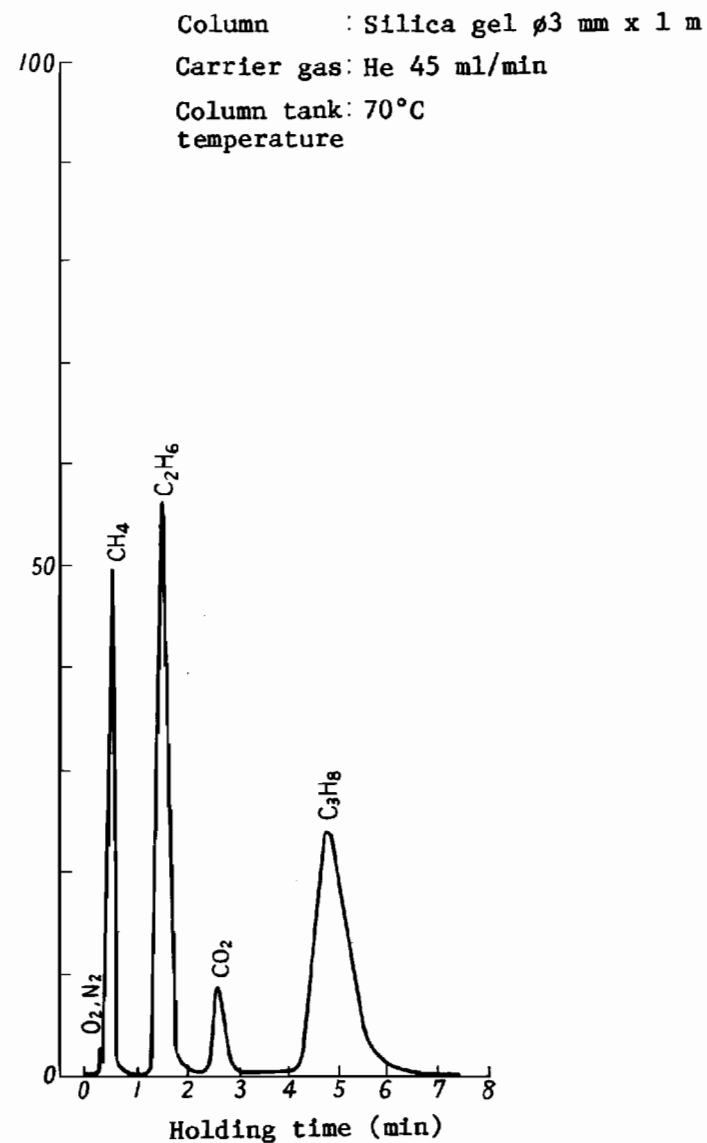


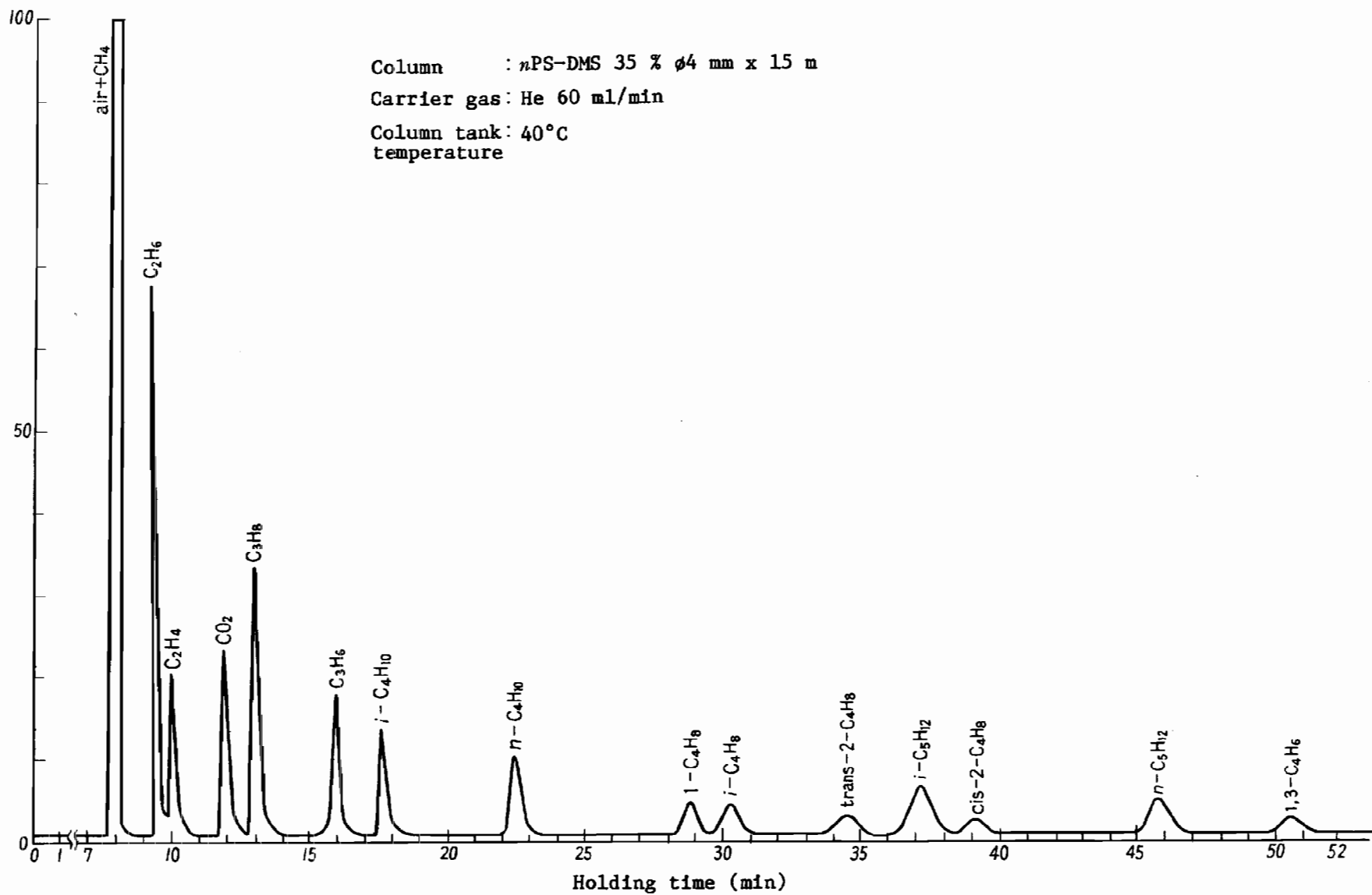
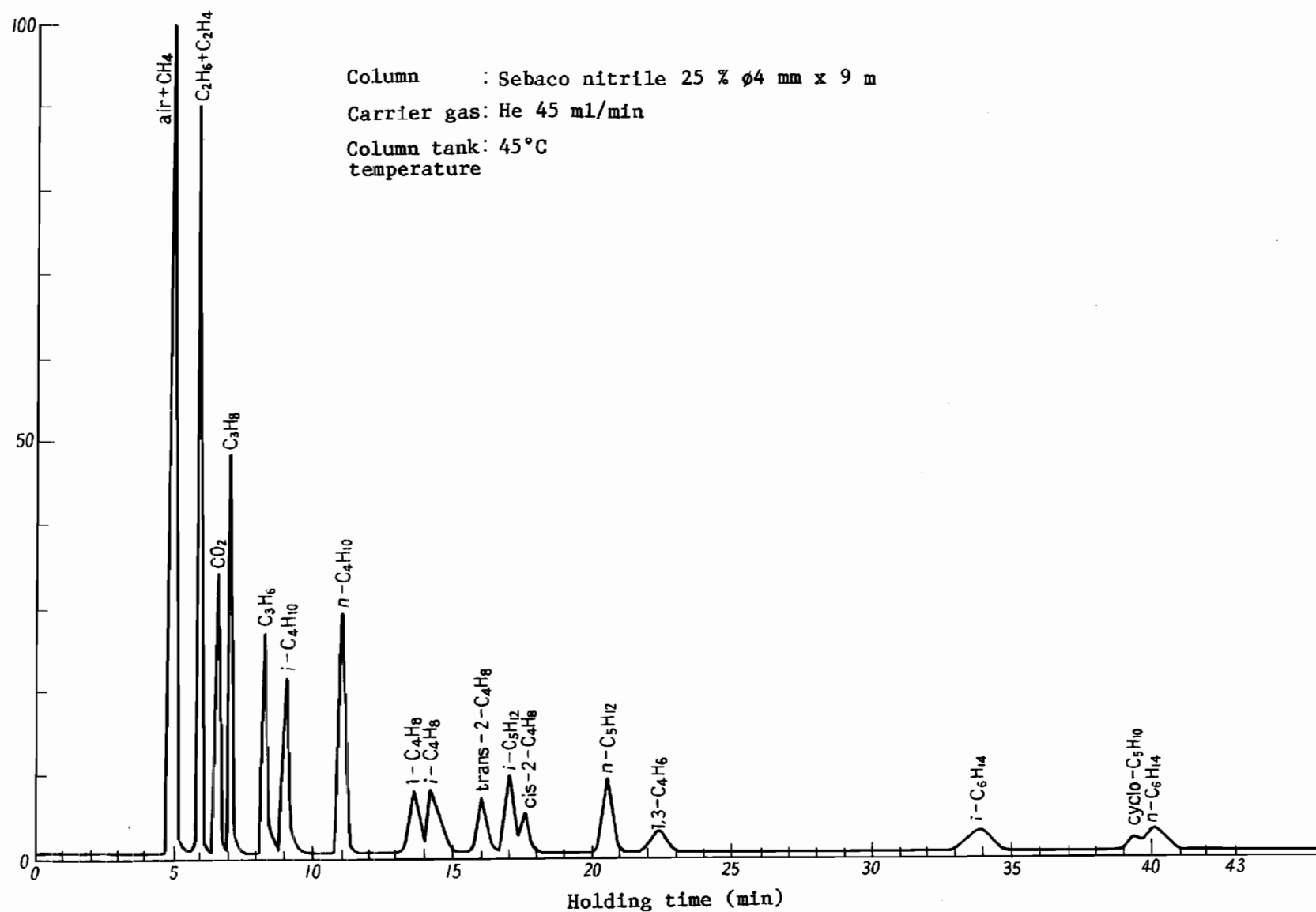
Fig. 12. Chromatogram on *n*PS-DMS (Example)

Fig. 13. Chromatogram on sebaco nitrile (Example)



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Fig. 14. Chromatogram on DOP (Example)

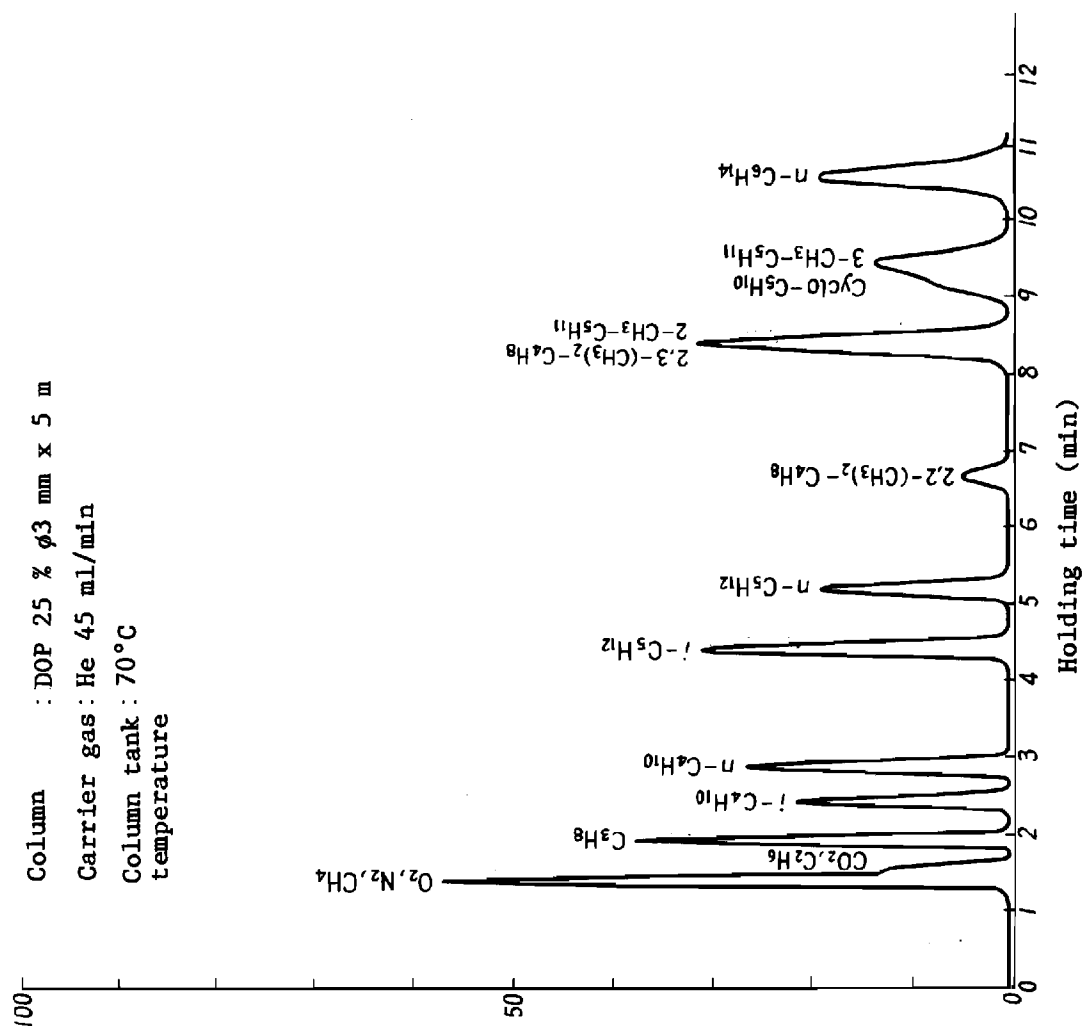


Fig. 15. Chromatogram on PEG6000 (Example)

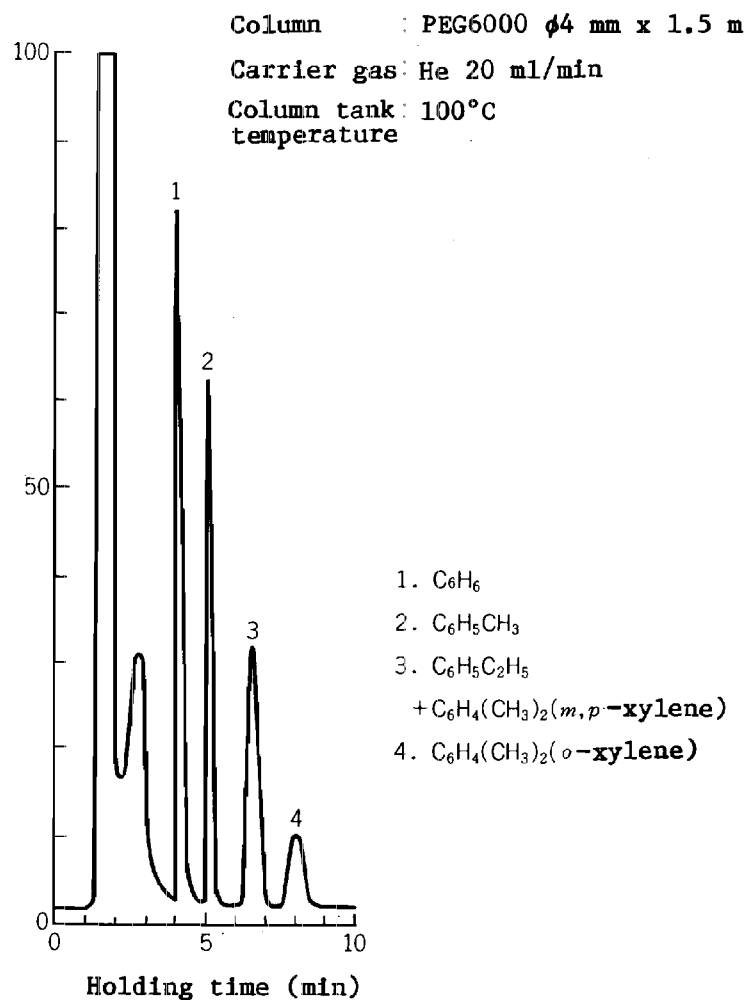


Fig. 16. Chromatogram on melt-silica capillary column (Example)

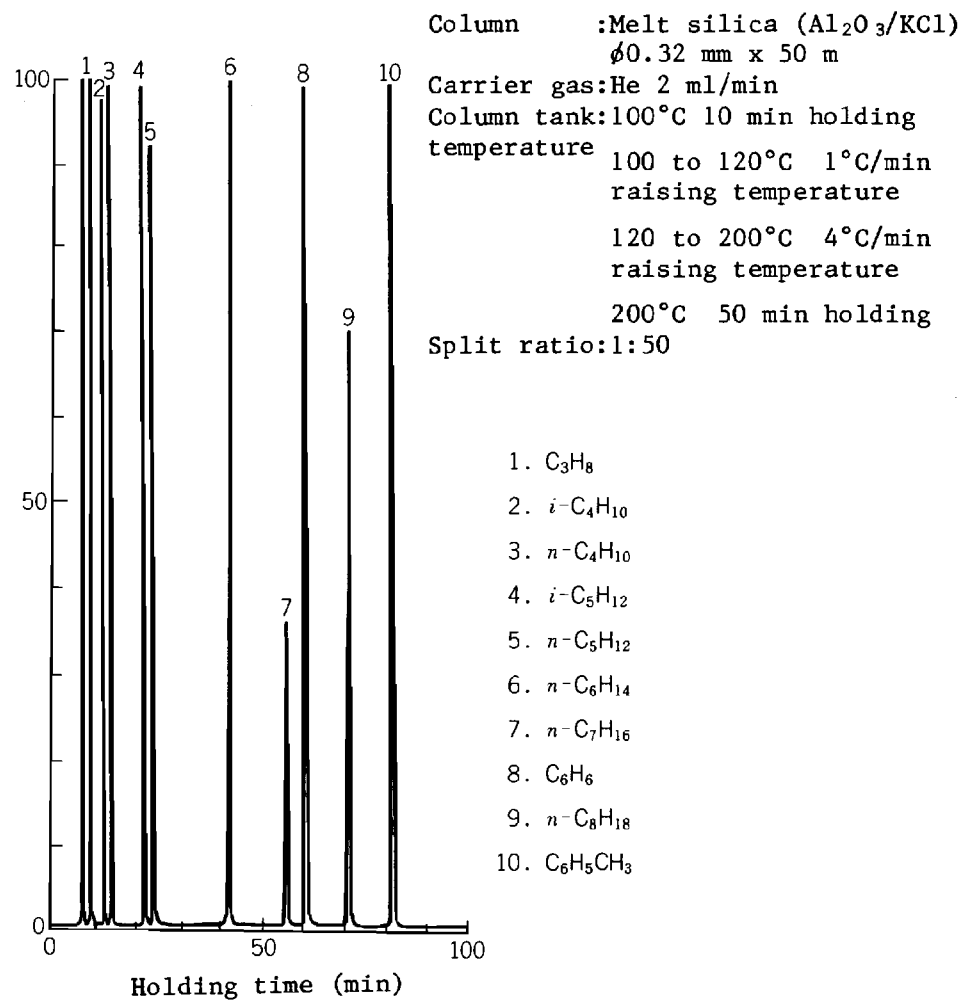
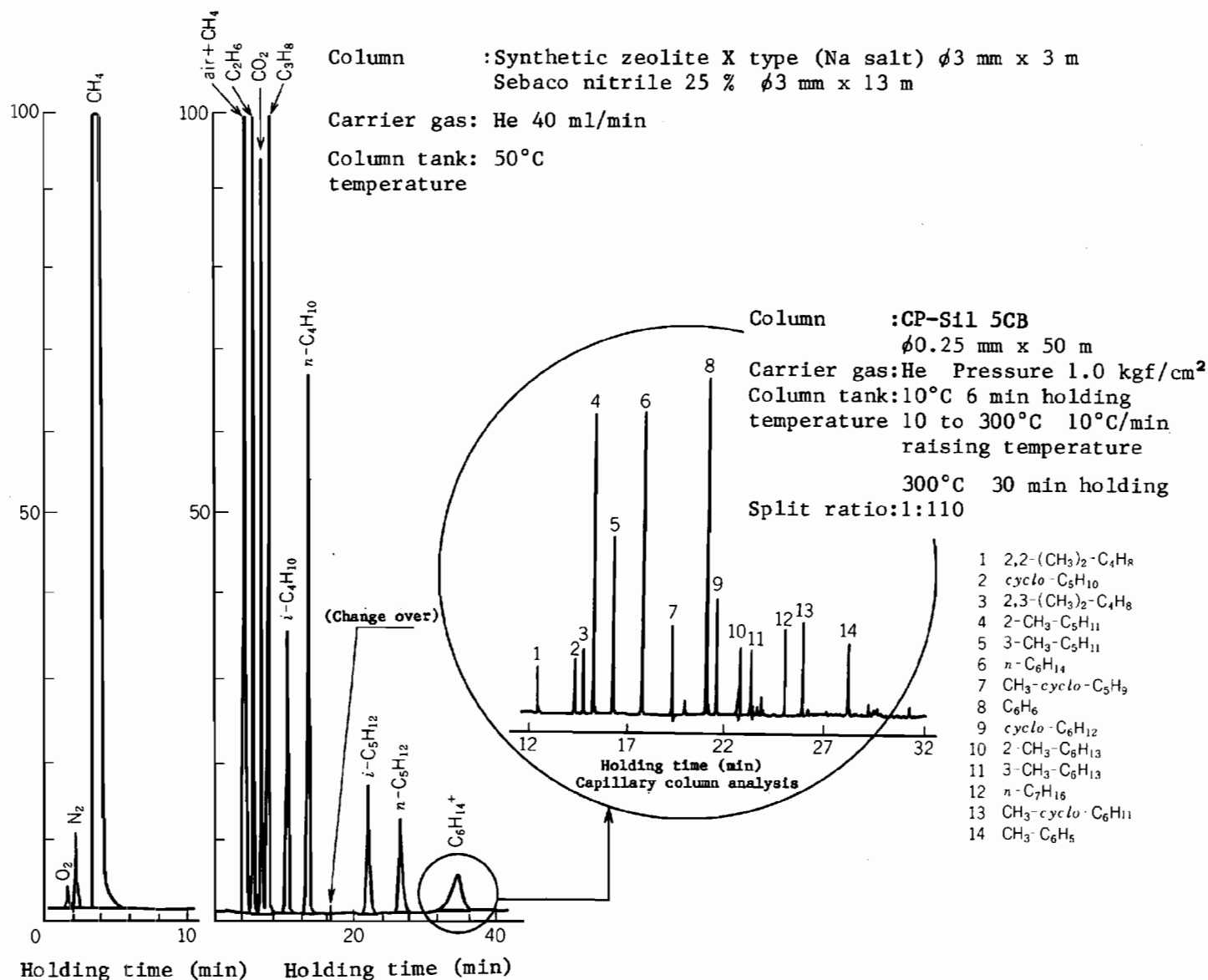


Fig. 17. Natural gas analysis used with back flushing (An example)



6. Analysis method for special constituent6.1 Division of special analysis constituents and analysis methods

Table 6. Division of analysis constituents and analysis methods

Analysis constituent	Analysis method
Total sulphur	Barium perchlorate precipitation titrimetric method Dimethyl sulphonazo. III absorptiometry
Hydrogen sulphide	Iodine titrimetric method Methylene blue absorptiometry Lead acetate test paper method
Ammonia	Neutralization titrimetric method Indophenol absorptiometry Silver nitrate - manganese nitrate test paper method
Naphthalene	Gas chromatography
Moisture content	Absorption weighing method Dew-point method

6.2 Analysis method of total sulphur6.2.1 Barium perchlorate precipitation titric method

(1) Summary Mix the sample gas with air or introduce into oxygen-hydrogen flame to burn, absorb the generated oxide of sulphur into hydrogen peroxide water, after making sulphuric acid, make pH about 6 with aqueous ammonia, add acetone, use dimethyl sulphonazo III as indicator and titrate with barium perchlorate solution. This method, in the case where sample gas of 100 l is taken, is capable of analyzing of gas not less than 0.01 g/m³ in total sulphur concentration.

(2) Reagents Reagents shall be as follows:

(2.1) Absorption liquid Hydrogen peroxide water (1+9)

This solution is preserved in a brown bottle.

(2.2) Aqueous ammonia (1+200)

(2.3) Potassium chloride solution Dissolve the potassium chloride 1 g specified in JIS K 8121 into water to make 100 ml.