International Standard ISO 6975

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Natural gas — Determination of hydrocarbons from butane (C_4) to hexadecane (C_{16}) — Gas chromatographic method

Gaz naturel — Détermination des hydrocarbures du butane (C_4) *jusqu'à l'hexadécane* (C_{16}) *— Méthode par chromatographie en phase gazeuse*

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6975 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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INTERNATIONAL STANDARD **ISO 6975-1986 (E)**

Natural gas — Determination of hydrocarbons from butane (C_4) to hexadecane (C_{16}) — Gas chromatographic method

1 Scope and field of application

This International Standard specifies a method of quantitative analysis of C_4 to C_{16} hydrocarbons in natural gas.

NOTES

1 C_4 and C_5 hydrocarbons are measured individually, and the higher hydrocarbons are grouped for each carbon number.

2 Complete analysis may be obtained by combining the results from this method with the unnormalized results from ISO 6974, which covers determination of helium, hydrogen, oxygen, nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8.

3 If used in conjunction with ISO 6974, the results for C_1 to C_8 are those obtained by means of the method described in ISO 6974; the results for C_9 to C_{16} are those obtained by means of the method described in this International Standard.

2 References

ISO 683/13, *Heat-treated steels, alloy steels and free-cutting steels — Part 13: Wrought stainless steels.*

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6974, *Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to* C_8 *— Gas chromatographic method.*

3 Principle

Injection of a natural gas sample on to a column, the packing of which has been impregnated with silicone oil. The separation is carried out using temperature programming and the constituents are detected by means of a flame ionization detector (FID).

Determination of quantitative results for the C_4 to C_{16} hydrocarbons either by calibrating the chromatograph with a calibration gas mixture containing butane and calculating all other hydrocarbon responses from this, or by applying the value for pentane obtained from ISO 6974 and calculating from this.

When the results are combined with those from ISO 6974, the total of the measured concentrations shall be normalized to 100 %.

NOTE — ISO 6974, with which the results from this analysis can be combined, uses two separations. These involve a molecular sieve 13 X [1] column with a thermal conductivity detector, and a Porapak R [1] column with a thermal conductivity and a flame ionization detector in series.

4 Materials

4.1 Carrier gas: helium, not less than 99,99 % pure[2], free from oxygen and water.

4.2 Auxiliary gases

4.2.1 Hydrogen, not less than 99,99 % pure.[2]

4.2.2 Air, free from hydrocarbon impurities.

4.3 Reference materials: 2-methylpropane, butane and all the straight chain alkanes from C_5 to C_{16}, all not less than 99 % pure.

4.4 Coolant: solid carbon dioxide or liquid nitrogen.

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[1] 13 X and Porapak R are trade names for commercially available products. At present, no other products intended for this purpose are known to be available commercially. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of these products by ISO.

[2] If the purity of the gas is less than that specified, it is essential to check that the type of impurity present does not interfere with the analysis. Also, even if the carrier gases argon and/or helium fall within the specification, some of the impurities present in these gases can nevertheless interfere with the analysis. Under these circumstances, appropriate purification is essential.

5 Apparatus

5.1 Gas chromatograph, capable of temperature programmed operation and equipped with an FID.

5.1.1 Column oven, capable of temperature programming from −50 to +300 °C at a rate of 10 ± 2 °C/min. To obtain and maintain a temperature of −50 °C an accessory for cooling either with liquid/solid carbon dioxide or with liquid nitrogen is necessary.

5.1.2 Flow regulator, to maintain the required carrier gas flow rate over the temperature programme range (see 5.1.1).

5.2 Injection devices

5.2.1 Gas sampling valve (bypass injector), capable of injecting sample volumes of 0,5 to 20 ml.

The choice of sample volume depends upon the limit of detection required. With a 0,5 ml sample loop the lower limit is 1 µmol/mol and the upper 5 % (mol/mol). With a 20 ml loop, the lower limit is 0,05 µmol/mol and the upper 0,1 % (mol/mol).

The sampling valve and the sample loop shall be maintained at a temperature of 100 ± 5 °C, to an accuracy of ± 0,5 °C.

5.2.2 Injection device, for liquids heated to 250 °C.

5.3 Column

5.3.1 Tube

- Material: stainless steel, number 20 according to ISO 683/13 (AISI type 316), cleaned and degreased
- Length: 3,6 m
- Internal diameter: 2 mm
- Form: appropriate to the chromatograph
- Radius: appropriate to the chromatograph

5.3.2 Packing

5.3.2.1 Methyl silicone phase on Chromosorb W, AW, DMCS treated, 180 to 250 µm (60 to 80 ASTM mesh): 10 g of liquid phase to 90 g of solid support.

5.3.2.2 Method of packing

Any method which results in uniform column packing may be used.

NOTE — The following method is suitable.

The column outlet is closed with a sintered disc or glass-wool plug. A reservoir containing rather more packing than is needed to fill the column is connected to the inlet and the packing is fed into the column by application of gas pressure, using nitrogen at a pressure of 0,4 MPa. The flow of packing into the column is assisted by vibration. When the column is full, allow the gas pressure to fall slowly to atmospheric pressure and then disconnect the reservoir.

5.3.3 Conditioning

Set the flow rate to the specified value. Programme the column temperature in such a way that it reaches 275 °C at a rate of 1 °C/min, and allow to stand overnight at this temperature. Leave the column disconnected from the detector during this conditioning.

When operated under the recommended conditions, the separations in each case should be at least as good as those shown in figures 1, 2 and 3.

To determine the resolution between octane and nonane use a calibration mixture of C_8 and C_9 hydrocarbons.

The resolution between octane and nonane is given by the formula

$$\frac{t_{C_9} - t_{C_8}}{W_{C_9} + W_{C_8}}$$

where

t_{C_8} is the absolute retention time, in seconds, of octane;

t_{C_9} is the absolute retention time, in seconds, of nonane;

W_{C_8} is the width of the peak, in seconds, at the baseline of the octane peak;

W_{C_9} is the width of the peak, in seconds, at the baseline of the nonane peak.

The value for this expression should be about 5.

5.4 Flame ionization detector (FID), with a time constant not greater than 0,1 s.

5.5 Thermostatted oven, for maintaining the sample cylinder at 75 ± 5 °C.

5.6 Sample cylinder, stainless steel, typical capacity 1 litre, rated for a pressure of 15 MPa at 100 °C.

5.7 Tubing, stainless steel, 0,7 to 1 mm inner diameter, to connect the sample cylinder to the gas sampling valve of the gas chromatograph, and capable of being heated to 100 °C.

5.8 Electrical trace heater, for maintaining the temperature of the needle valve of the sample cylinder at approximately 100 °C. Other suitable means of heating may also be used.

5.9 Potentiometric recorder

- Range: appropriate to the detector (usually 1 to 10 mV)
- Impedance: appropriate to the detector (usually 2 000 Ω)
- Response time: ⩽ 0,5 s

NOTE — Alternative devices of equivalent response may be used.

5.10 Integrator

Wide range: 0 to 1 V

The integrator shall be capable of baseline tracking and of measuring peaks on a sloping baseline.

6 Samples

6.1 Composition

The sample is a natural gas containing components which usually fall within the ranges listed in table 1.

Table 1 — Concentration ranges of natural gas components

Component	Range [% (mol/mol)]	Test method	
Helium	0,01 to 0,5	ISO 6974	
Hydrogen	0,01 to 0,5	ISO 6974	
Oxygen	0,1 to 0,5	ISO 6974	
Nitrogen	0,1 to 40	ISO 6974	
Carbon dioxide	0,1 to 30	ISO 6974	
Methane	50 to 100	ISO 6974	
Ethane	0,1 to 15	ISO 6974	
Propane	0,001 to 5	ISO 6974	
Butanes	0,001 to 0,5	ISO 6974	ISO 6975
Pentanes	0,001 to 0,5	ISO 6974	ISO 6975
Hexanes, benzene	0,001 to 0,5	ISO 6974	ISO 6975
Heptanes, toluene	0,001 to 0,5	ISO 6974	ISO 6975
C_8	0,000 1 to 0,1	ISO 6974	ISO 6975
C_9 to C_{16}, each	0,000 1 to 0,05		ISO 6975

6.2 Sampling precautions

Ascertain that the pressure rating of the sampling cylinder is adequate.

The sample should be taken into a high-pressure cylinder equipped with valves at both ends. Preferably first flush the cylinder with at least 20 times its own volume of the gas to be analysed.

The sample line and cylinder should be kept at a temperature which is at least equal to, but preferably slightly higher than, the flowline temperature while sampling is taking place. In order to avoid condensate formation in the cylinder or its connecting line, any pressure drop across the sampling system should be minimal. A suitable cylinder and the connecting line configuration are shown in figure 4 and operating instructions are given in the annex.

7 Procedure

7.1 Setting up the apparatus

7.1.1 Injector

Set the temperature of the gas sampling valve and the sampling loop to 100 ± 5 °C to an accuracy of ± 0,5 °C.

This temperature shall not be lower than the temperature of the needle valve and the transfer lines.

7.1.2 Oven and column

7.1.2.1 Oven temperature programme

a) initial temperature: −50 ± 10 °C for 2 min;

b) heat at 10 ± 2 °C/min to 250 ± 10 °C;

c) maintain at 250 ± 10 °C for 10 min.

NOTE — When using a 0,5 ml sample loop, the starting temperature of the temperature programme may be increased to +40 °C. In that case no accessory for cooling the column oven is necessary.

7.1.2.2 Carrier gas flow rate

25 ml/min.

7.1.3 Detector

Set the temperature to 260 ± 10 °C.

Adjust the hydrogen and air flow rates in accordance with the manufacturer's instructions so as to give optimum response.

Ignite the gas mixture in the detector, taking suitable precautions in using a mixture of hydrogen and air.

7.1.4 Sample cylinder

Maintain the sample cylinder at a temperature of 75 ± 5 °C for about 24 h and the cylinder needle valve at a temperature of 100 ± 5 °C for at least 1 h before starting to introduce the sample.

7.1.5 Transfer lines

Connect the sample cylinder to the gas sample valve with stainless steel tubing of inner diameter 0,7 to 1 mm.

Maintain the tubing at a temperature of 100 ± 5 °C using an electrical trace heater.

7.1.6 Recorder

Set the chart speed to a minimum of 5 mm/min.

7.1.7 Integrator

Set up the integrator in accordance with the manufacturer's instructions.

7.2 Identification

Prepare a suitable mixture of all straight chain alkanes from C_5 to C_{16} (4.3) and inject 0,2 µl of this mixture into the gas chromatograph using operating conditions identical to those specified for the sample.

7.3 Calibration

The instrument is calibrated either by using a calibration gas mixture of butane in methane, or, when the results are to be combined with those from ISO 6974, by using the bridge component (pentane), whose concentration in the sample has been established by means of the method described in ISO 6974.

7.3.1 External calibration using calibration gas mixture

7.3.1.1 Use a calibration gas mixture (table 2) prepared by means of the method described in ISO 6142.

Table 2 — Calibration gas mixture

Component	Concentration values in % (mol/mol)
Butane	Expected concentration ± 50 % in sample, but in any case not less than 0,1 %
Methane	Balance

7.3.1.2 Inject the calibration gas mixture, if possible, immediately before or immediately after each analysis. When analyses are being performed continuously, inject the calibration gas mixture at least once every 2 h.

7.3.2 Bridge component

Use the known concentration of pentane, calculated in accordance with ISO 6974, as a bridge component to calculate the concentrations of C_9 to C_{16} (see 8.1.2).

7.4 Test

7.4.1 Using the gas sampling valve, inject a portion of the sample to be analysed ensuring that it reaches the required conditions of temperature and pressure in the loop before it is injected. If using an external standard, inject the appropriate mixture under the same conditions.

7.4.2 Flush the sample loop at, or close to, atmospheric pressure by a volume of sample equal to approximately 20 times the volume of the sample loop.

NOTE — In certain cases, for example samples under atmospheric or sub-atmospheric pressure, the procedure may be modified as follows.

Evacuate the injector and connecting tubing and allow the gas to enter until the pressure reaches a constant value which has to be read from a manometer.

7.5 Examination of the chromatogram

7.5.1 Typical chromatograms are given in figures 1, 2 and 3. Figures 1 and 2 are obtained using a 0,5 ml sample volume and starting temperatures of −50 °C and +40 °C respectively. Figure 3 is obtained using a 20 ml sample volume and starting temperature of −50 °C.

7.5.2 The positions of the straight chain alkanes may be determined by comparison with synthetic mixtures of these compounds, injected as liquids. The total concentration of material corresponding to a particular carbon number is taken as the total area of the peaks eluting after the straight chain alkanes of the previous lower carbon number up to and including the straight chain alkane of that carbon number.

This is an approximation, as up to C_8 the aromatics and some naphthenes elute after the straight chain alkane of the same number. Moreover, for C_9 and heavier, the number of exceptions increases with the carbon number.

8 Expression of results

This method allows the determination of the concentrations of the hydrocarbons from C_4 to C_{16}.

The concentration of the components shall be given as mole fraction, expressed as a percentage, to three significant figures for mole ratios greater than or equal to 0,1 %, and to two significant figures for lower mole ratios.

The lower limit of detection depends on the amount of sample introduced (see 5.2.1).

8.1 Calculation

8.1.1 If an external standard has been used, measure the areas of the peaks due to components in both standard and sample.

Calculate the concentrations, $X_{i,n}$, the mole ratio, expressed as a percentage, of substance i of carbon number n, in the sample, according to the equation

$$X_{i,n} = X_{\mathrm{c},4} \left(\frac{4A_{i,n}}{nA_{\mathrm{c},4}} \right)$$

where

$X_{\mathrm{c},4}$ is the mole ratio, expressed as a percentage, of butane in the calibration gas mixture;

$A_{i,n}$ is the area of the peak due to substance i from the chromatogram of the sample;

$A_{\mathrm{c},4}$ is the area of the peak due to butane from the calibration gas mixture.

8.1.2 If the method specified in this International Standard is used with that in ISO 6974, the unnormalized results obtained from ISO 6974 shall be combined with the results obtained from this International Standard. The results of the two analyses shall be combined in one test report. Pentane is used as a bridge component and the concentrations, $X_{i,n}$, the mole ratio, expressed as a percentage of substances i of carbon number n (where $9 < n < 16$), in the sample, are calculated from the equation

$$X_{i,n} = X_5 \left(\frac{5A_{i,n}}{nA_5} \right)$$

where

X_5 is the mole ratio, expressed as a percentage, of pentane in the sample as determined by ISO 6974;

$A_{i,n}$ is the area of the peak due to substance i from the chromatogram of the sample;

A_5 is the area of the peak due to pentane from the sample.

If the sum of the mole ratio expressed to the nearest 0,001 % adds up to between 99 and 101 %, the mole ratios shall be normalized to 100,000 %. If not, the sample shall be re-analysed.

8.2 Precision

The reproducibility of the method specified in this International Standard has not been determined.

9 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) all information necessary for complete identification of the sample, for example:

- the date and time of sampling into the cylinder,
- the place in the pipeline system at which the sample was taken,
- the conditions of the gas in the pipeline system, such as temperature, pressure and throughput;

c) the sampling method used (including the size and type of material and the temperature of the high-pressure cylinder);

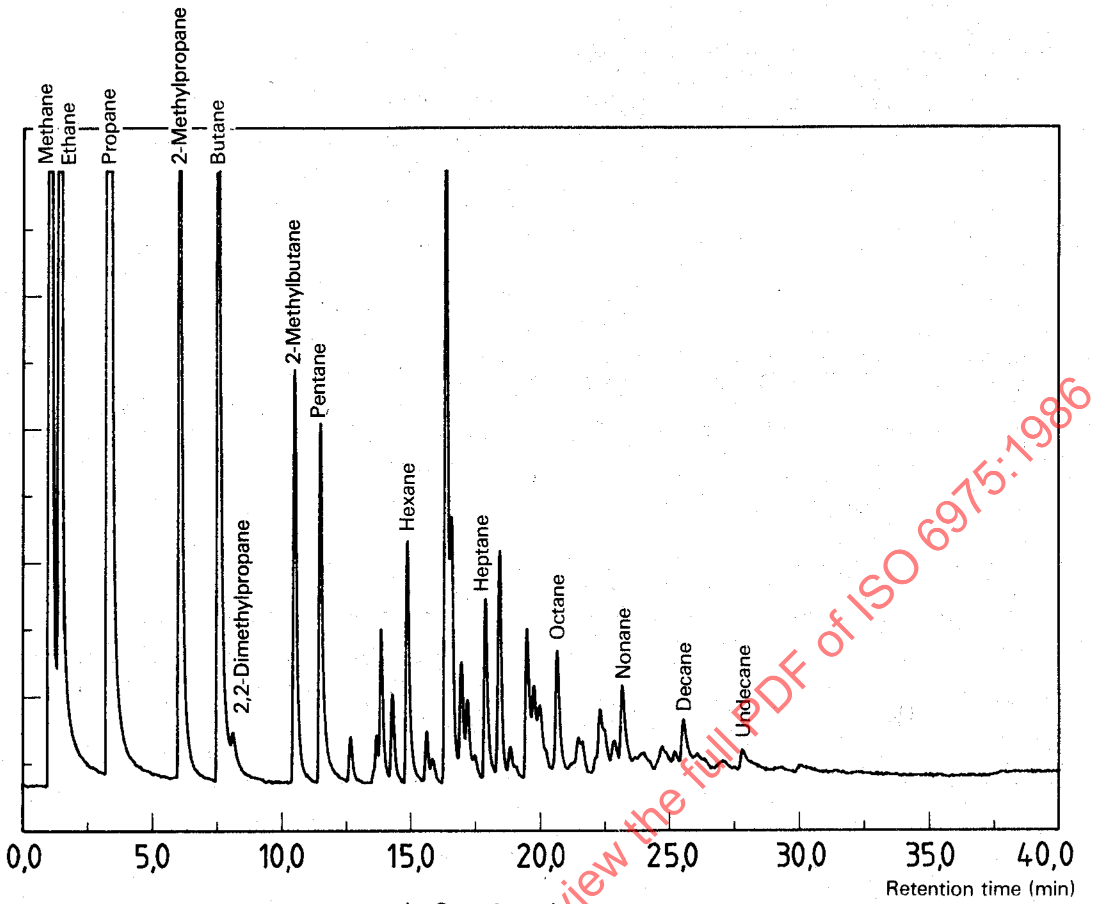
d) any deviation from the procedure specified;

e) a complete list of all components determined or detected;

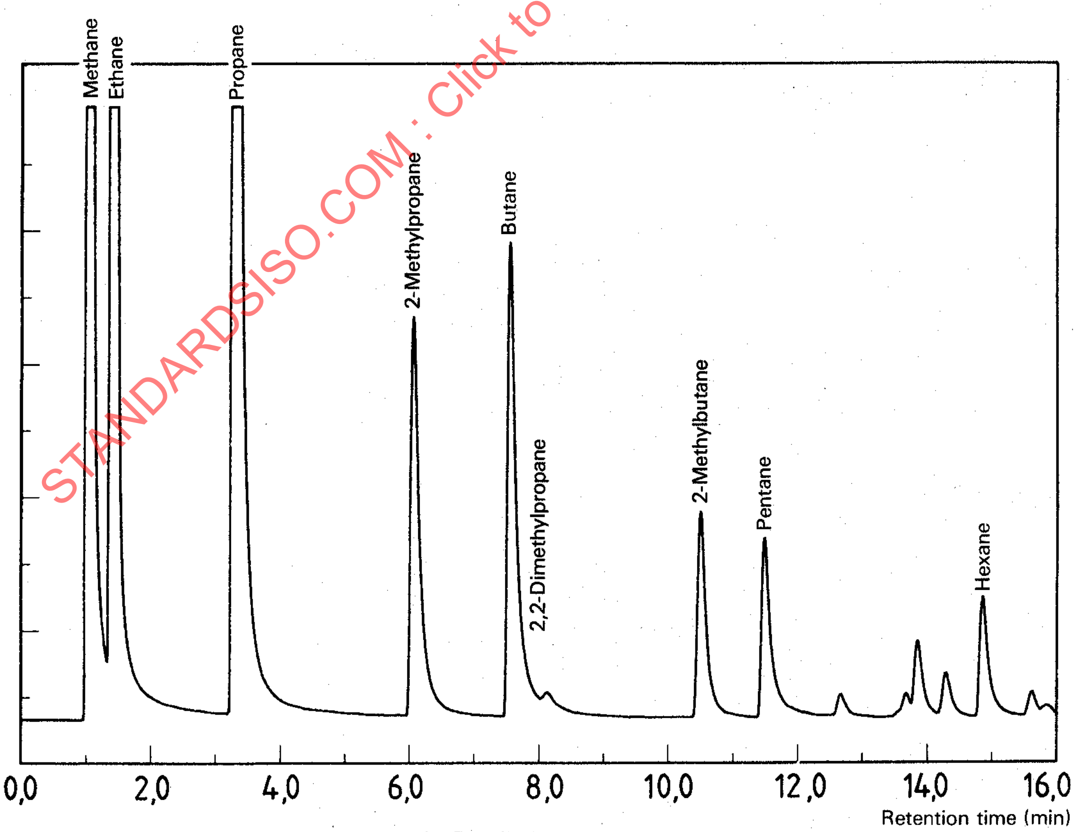
f) the concentrations determined;

g) if possible, the precision of the determined concentrations of the components of the sample, including the number of determinations;

h) any unusual features noted during the determination (i.e. in the chromatogram).



a) **Complete chromatogram**



b) **Detail chromatogram**

Figure 1 — Chromatogram of a natural gas
(Starting temperature: -50 °C; sample volume: 0,5 ml)