# INTERNATIONAL STANDARD

# ISO 6974-6

First edition
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# Natural gas — Determination of composition with defined uncertainty by gas chromatography —

## Part 6:
## Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and $C_1$ to $C_8$ hydrocarbons using three capillary columns

*Gaz naturel — Détermination de la composition avec une incertitude définie par chromatographie en phase gazeuse —*

*Partie 6: Détermination de l'hydrogène, de l'hélium, de l'oxygène, de l'azote, du dioxyde de carbone et des hydrocarbures ($C_1$ à $C_8$) en utilisant trois colonnes capillaires*

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this part of ISO 6974 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 6974-6 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This first edition of ISO 6974-6, together with ISO 6974-1, ISO 6974-2, ISO 6974-3, ISO 6974-4 and ISO 6974-5, cancels and replaces ISO 6974:1984 which specified only one method.

ISO 6974 consists of the following parts, under the general title *Natural gas — Determination of composition with defined uncertainty by gas chromatography*:

⎯ *Part 1: Guidelines for tailored analysis*

⎯ *Part 2: Measuring-system characteristics and statistics for processing of data*

⎯ *Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to $C_8$ using two packed columns*

⎯ *Part 4: Determination of nitrogen, carbon dioxide and $C_1$ to $C_5$ and $C_{6+}$ hydrocarbons for a laboratory and on-line measuring system using two columns*

⎯ *Part 5: Determination of nitrogen, carbon dioxide and $C_1$ to $C_5$ and $C_{6+}$ hydrocarbons for a laboratory and on-line process application using three columns*

⎯ *Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and $C_1$ to $C_8$ hydrocarbons using three capillary columns*

Annex A of this part of ISO 6974 is for information only.

# Introduction

This part of ISO 6974 describes a precise and accurate method for the analysis of natural gas, which permits the determination of the composition of natural gas. The compositional data obtained are used for the calculation of calorific value, relative density and Wobbe index.

This method requires the use of three columns which are put in two gas chromatographs.

Due to the high separation power of the capillary columns used, components, generally not present in natural gas but in some natural gas substitutes, can also be detected using this method. For the analysis of natural gas substitutes, a methanizer is used in addition.

This part of ISO 6974 provides one of the methods that may be used for determining the composition of natural gas in accordance with parts 1 and 2 of ISO 6974.

# Natural gas — Determination of composition with defined uncertainty by gas chromatography —

## Part 6:
## Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and $C_1$ to $C_8$ hydrocarbons using three capillary columns

## 1 Scope

This part of ISO 6974 describes a gas chromatographic method for the quantitative determination of the content of hydrogen, helium, oxygen, nitrogen, carbon dioxide and $C_1$ to $C_8$ hydrocarbons in natural gas samples using three capillary columns. It is applicable to the analysis of gases containing constituents within the mole fraction ranges given in Table 1 and is commonly used for laboratory applications. These ranges do not represent the limits of detection, but the limits within which the stated precision of the method applies. Although one or more components in a sample may not be present at detectable levels, the method can still be applicable.

This part of ISO 6974 is only applicable if used in conjunction with parts 1 and 2 of ISO 6974.

This method can also be applicable to the analysis of natural gas substitutes.

NOTE      Additional information on the applicability of this method to the determination of natural gas substitutes is also given where relevant.

## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this part of ISO 6974. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this part of ISO 6974 are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6974-1:2000, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis*

ISO 6974-2, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for processing of data*

ISO 7504, *Gas analysis — Vocabulary*

**Table 1 — Application ranges**

| Component | Formula | Mole fraction % | | |
|---|---|---|---|---|
| Helium | He | 0,002 | to | 0,5 |
| Hydrogen | $H_2$ | 0,001 | to | 0,5 |
| Oxygen | $O_2$ | 0,007 | to | 5 |
| Nitrogen | $N_2$ | 0,007 | to | 40 |
| Methane | $CH_4$ | 40 | to | 100 |
| Carbon monoxide [a] | CO | 0,001 | to | 1 |
| Carbon dioxide | $CO_2$ | 0,001 | to | 10 |
| Ethyne (Acetylene) [a] | $C_2H_2$ | 0,001 | to | 0,5 |
| Ethene [a] | $C_2H_4$ | 0,001 | to | 0,5 |
| Ethane | $C_2H_6$ | 0,002 | to | 15 |
| Propene [a] [b] | $C_3H_6$ | 0,001 | to | 0,5 |
| Propane [b] | $C_3H_8$ | 0,001 | to | 5 |
| *i*-Butane | $C_4H_{10}$ | 0,000 1 | to | 1 |
| *n*-Butane | $C_4H_{10}$ | 0,000 1 | to | 1 |
| 2,2-Dimethylpropane (Neopentane) | $C_5H_{12}$ | 0,000 1 | to | 0,5 |
| 2-Methylbutane (*i*-Pentane) | $C_5H_{12}$ | 0,000 1 | to | 0,5 |
| *n*-Pentane | $C_5H_{12}$ | 0,000 1 | to | 0,5 |
| Cyclopentane | $C_5H_{10}$ | 0,000 1 | to | 0,5 |
| 2,2-Dimethylbutane | $C_6H_{14}$ | 0,000 1 | to | 0,5 |
| 2,3-Dimethylbutane | $C_6H_{14}$ | 0,000 1 | to | 0,5 |
| 2-Methylpentane | $C_6H_{14}$ | 0,000 1 | to | 0,5 |
| 3-Methylpentane | $C_6H_{14}$ | 0,000 1 | to | 0,5 |
| *n*-Hexane | $C_6H_{14}$ | 0,000 1 | to | 0,5 |
| Benzene | $C_6H_6$ | 0,000 1 | to | 0,5 |
| Cyclohexane | $C_6H_{12}$ | 0,000 1 | to | 0,5 |
| Heptanes [c] | $C_7H_{16}$ | 0,000 1 | to | 0,5 |
| Methylcyclohexane | $C_7H_{14}$ | 0,000 1 | to | 0,5 |
| Toluene | $C_7H_8$ | 0,000 1 | to | 0,5 |
| Octanes [d] | $C_8H_{18}$ | 0,000 1 | to | 0,5 |
| Xylenes [e] | $C_8H_{10}$ | 0,000 1 | to | 0,5 |

NOTE     The analysis may be extended under specific conditions (e.g. greater sample volume) to hydrocarbons heavier than $C_8$, if present in mole fractions > 1 µmol/mol.

[a]     These components are generally not present in natural gas, but in natural gas substitute.

[b]     The separation of propane from propene is critical. Depending on the column in use this separation may not be achieved.

[c]     Components included: *n*-heptane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2,2,3-trimethylbutane. Not all isomers can be separated from each other.

[d]     Components included: *n*-octane, 2-methylheptane, 3-methylheptane, 4-methylheptane, dimethylcyclohexanes, 2,2-dimethylhexane, 2,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, 3,3-dimethylhexane, 3,4-dimethylhexane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane (*i*-octane), 2,3,3-trimethylpentane, 2,3,4-trimethylpentane, 2,2,3,3-tetramethylbutane. Not all isomers can be separated from each other.

[e]     Components included: *o*-xylene, *m*-xylene, *p*-xylene. *m*- and *p*-xylene will not be separated from each other.

# 3   Principle

## 3.1   Analysis of natural gas samples

Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons from $C_1$ to $C_8$ by gas chromatography using three capillary columns. A PLOT[1] precolumn is used for the separation of carbon dioxide ($CO_2$) and ethane ($C_2H_6$).

A molecular sieve PLOT column is used for the separation of the permanent gases helium (He), hydrogen ($H_2$), oxygen ($O_2$), nitrogen ($N_2$) and methane ($CH_4$).

A thick film WCOT[2] column coated with an apolar phase is used for the separation of the $C_3$ to $C_8$ (and heavier) hydrocarbons.

The permanent gases helium (He), hydrogen ($H_2$), oxygen ($O_2$), nitrogen ($N_2$) and methane ($CH_4$) are detected with a thermal conductivity detector (TCD). The $C_2$ to $C_8$ hydrocarbons are detected with a flame ionization detector (FID).

## 3.2   Analysis of natural gas substitutes

Carbon monoxide (CO) and carbon dioxide ($CO_2$) are detected using an FID after reduction of the components to $CH_4$ by a methanizer. Use of a methanizer, makes it possible to detect CO and $CO_2$ at a mole fractions greater than 0,001 %. If the samples do not include CO or $CO_2$ or if the CO and/or the $CO_2$ mole fraction exceeds 0,02 %, a methanizer is not required. CO and $CO_2$ may then alternatively be detected with the TCD.

When analysing natural gas substitutes, the PLOT column described in 3.1 can also be used for the separation of ethyne ($C_2H_2$) and ethene ($C_2H_4$) and the molecular sieve PLOT column can also be used for the analysis of carbon monoxide (CO).

# 4   Materials

## 4.1   Carrier gases

**4.1.1**   **Argon** (Ar), $\geqslant$ 99,999 % pure, free from oxygen and water.

**4.1.2**   **Nitrogen** ($N_2$), $\geqslant$ 99,999 % pure or **Helium** (He) $\geqslant$ 99,999 % pure.

## 4.2   Auxiliary gases

**4.2.1**   **For FID detection:**

**4.2.1.1**     **Nitrogen** ($N_2$) or **helium** (He), $\geqslant$ 99,996 % pure.

**4.2.1.2**     **Air**, free from hydrocarbon impurities, i.e. the mole fraction of hydrocarbons $< 1 \times 10^{-4}$ %.

**4.2.1.3**     **Hydrogen** ($H_2$), $\geqslant$ 99,999 % pure, free from corrosive gases and organic compounds.

**4.2.2**   **For methanizer** (optional), when analysing natural gas substitutes:

**4.2.2.1**     **Hydrogen,** $\geqslant$ 99,999 % pure (may also be used as make up gas).

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1)   Porous layer open tubular

2)   Wall coated open tubular

**4.2.2.2    Pressurized laboratory air**, for the operation of pneumatically actuated valves.

### 4.3    Reference materials

**4.3.1    Working reference gas mixture** (WRM), the composition of which shall be chosen to be similar to the anticipated composition of the sample.

Mole fractions of the components shall not differ by more than the relative deviations stated in Table 2.

A cylinder of distributed natural gas, containing all the components measured by this method may also be used as the WRM. Prepare the WRM in accordance with ISO 6142 and/or certify it in accordance with ISO 6143. The WRM shall contain at least nitrogen, carbon dioxide, methane, ethane, propane, *i*-butane, *n*-butane. In the case of an indirect determination, the working reference gas mixture shall contain the reference component with a concentration in agreement with the expected concentration range. Consequently, it may be necessary to use more than one WRM.

**Table 2 — Relative deviation between sample and WRM**

| Sample<br>mole fraction (%) | WRM<br>relative deviation (%) |
|:---:|:---:|
| 0,001 to 0,1 | ± 100 |
| 0,1 to 1 | ± 50 |
| 1 to 10 | ± 10 |
| 10 to 50 | ± 5 |
| 50 to 100 | ± 3 |

**4.3.2    Performance test gases.**

**4.3.2.1    For methanizer operation** (optional), consisting of a volume fraction of 0,001 % to 0,02 % each of $CH_4$, CO and $CO_2$ in helium, for use when analysing natural gas substitutes.

**4.3.2.2    Gas containing benzene and cyclohexane**, for use in verifying peak resolution.

**4.3.2.3    Gas containing hydrogen and helium**, for use in verifying peak resolution.

## 5    Apparatus

**5.1    Gas chromatograph system(s),** consisting of the following components:

**5.1.1    Two column ovens**, for temperature-programmed operation, capable of following a given linear temperature gradient (see Table 3).

The columns may either be installed in a dual-oven gas chromatograph or in two separate instruments. The analyser should be capable of independently controlling the temperatures of both column ovens.

**5.1.1.1    Instrument 1 oven,** containing the PLOT precolumn and the molecular sieve column (see Figures 1, 2 and 3).

Instrument 1 may alternatively be equipped with a column oven for isothermal operation for a temperature range from 40 °C to 140 °C and capable of maintaining the temperature to within ± 0,1 °C at any point inside the oven chamber.

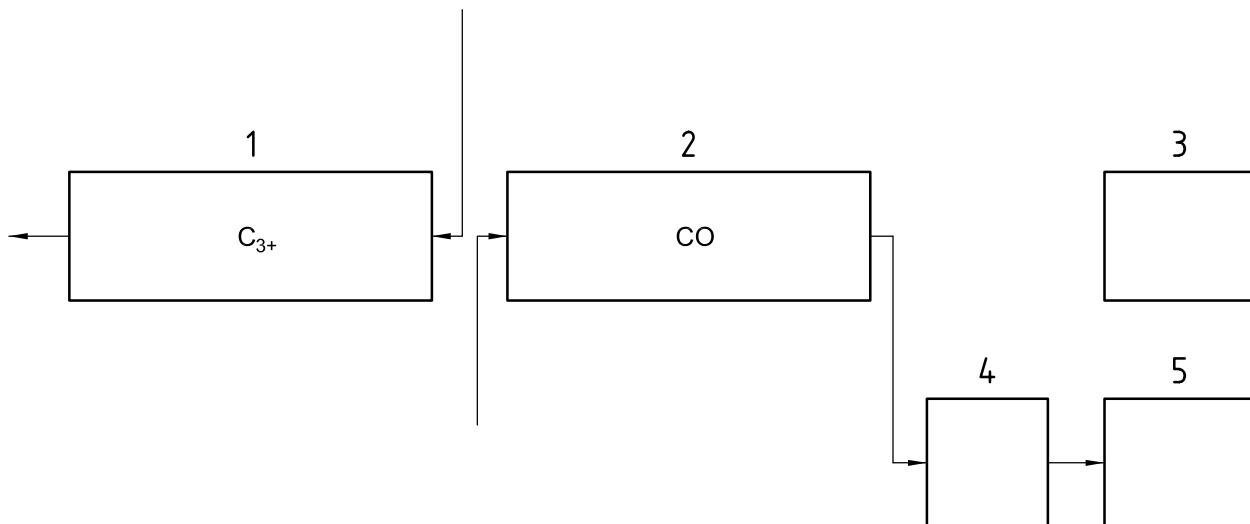**5.1.1.2    Instrument 2 oven,** containing the WCOT column.

**Key**
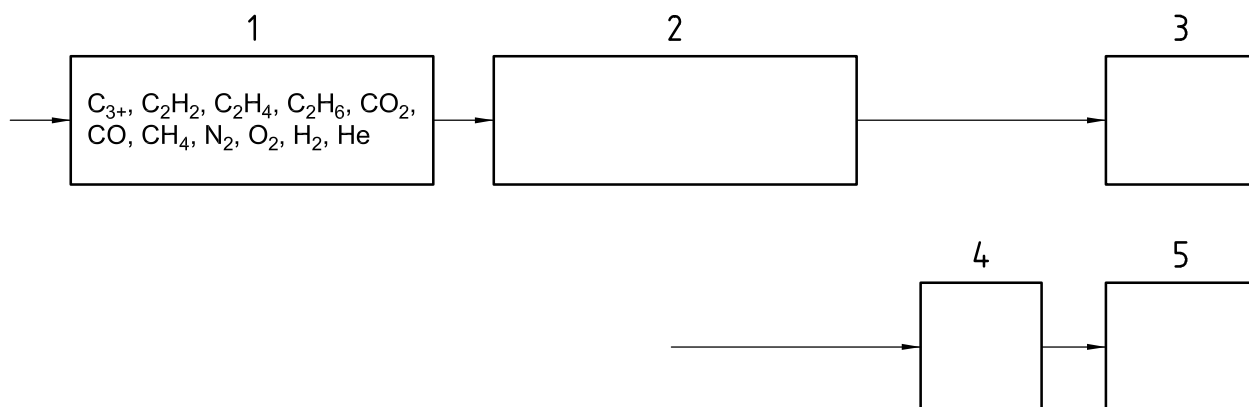
1   Plot precolumn
2   Molecular sieve Plot column
3   TCD
4   Methanizer
5   FID

**Figure 1 — Schematic diagram of the column configuration at the time of sample injection**



**Key**
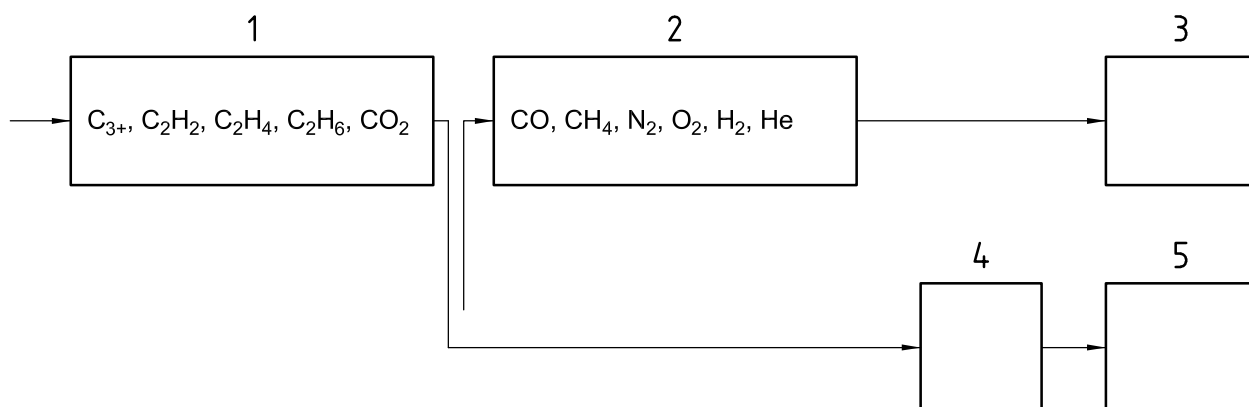
1   Plot precolumn
2   Molecular sieve PLOT column
3   TCD
4   Methanizer
5   FID

**Figure 2 — Schematic diagram of the column configuration for the determination of $CO_2$ and $C_2$**

**Key**

1 Plot precolumn
2 Molecular sieve PLOT column
3 TCD
4 Methanizer
5 FID

**Figure 3 — Schematic diagram of the column configuration for the determination
of CO and backflushing of $C_{3+}$ hydrocarbons**

**5.1.2 Flow regulators**, providing suitable flow rates for capillary columns.

**5.1.3 Gas sampling valves** (GSV), maintained at a constant temperature to within $\pm$ 0,5 °C.

Sample loop volumes of about 0,25 ml may be used in conjunction with capillary split devices. Alternatively, microvalves with internal sample loops may be used without split devices.

**5.1.4 Valveless** or **micro-valve column-switching system**, suitable for backflushing.

Examples of possible configurations of the column switching system are shown in Figure 4 and Figure 5.

**5.1.5 Thermal conductivity detector** (TCD) and **flame ionization detector** (FID), having a time constant and internal volume appropriate for operation with capillary columns. For analyses performed on two separate gas chromatographs, the instruments shall be equipped as follows:

**5.1.5.1 Instrument 1 detectors**: **TCD** and an **FID**.

**5.1.5.2 Instrument 2 detector:** an additional **FID**.

**5.1.6 Data acquisition system**, of suitable resolution and time constant, capable of automatic registration of analyses.

**5.1.7 Methanizer** (optional), to catalytically reduce on-line carbon monoxide (CO) and carbon dioxide ($CO_2$) to $CH_4$ when analysing natural gas substitutes.

These components can then be detected sensitively by the FID. A methanizer is not required if the samples do not contain CO.

If a methanizer is not installed, $CO_2$ and $C_2H_6$ are detected using the reference cell of the TCD (Figure 5), thus giving reversed (negative) peaks for these components. All other components are backflushed from the precolumn.

Determine the conversion efficiency of the methanizer (nickel catalyst) by injecting a test sample containing a known amount (volume fraction of 0,001 % to 0,02 %) of methane, carbon monoxide and carbon dioxide. If necessary, adjust the catalyst temperature to optimize conversion efficiency and peak symmetry. Also adjust the $H_2$ flow to optimize sensitivity. Under optimum operating conditions the methanizer has a conversion efficiency of nearly 100 %. It is recommended to determine the stability of the methanizer.

Small amounts of $H_2S$ and probably other sulfur compounds reaching the methanizer cause immediate deactivation of the catalyst bed. For this reason $H_2S$ shall be cut off by suitable column switching. A poisoned catalyst is identified by the onset of tailing on both CO and $CO_2$ peaks.

A periodic verification of the absence of leak is recommended. This can be performed by verifying that the injection of the carrier gas does not lead to any nitrogen or oxygen peak.

**5.2    Capillary columns**, consisting of the following:

**5.2.1    PLOT fused silica capillary precolumn**, for the separation of air, $CO_2$, $C_2H_2$, $C_2H_4$, $C_2H_6$ and $C_3H_8$.

Sufficient resolution between $CH_4$ and $CO_2$ is required to enable column switching.

A 25 m $\times$ 0,53 mm i.d., with a 20 µm phase thickness, PoraPLOT U[3] column is recommended because it provides good separation of these components.

**5.2.2    Molecular sieve PLOT fused silica capillary column** for the separation of He, $H_2$, $O_2$, $N_2$, $CH_4$ and CO.

Test the separation efficiency of this column by injecting a test sample of $H_2$ with a mole fraction of 4 % and of He with a mole fraction of 0,05 %. The separation efficiency should be sufficient to determine quantitatively both components and shall meet the peak resolution requirement given in clause 7.1.

A 25 m $\times$ 0,53 mm i.d., with a 50 µm phase thickness, molecular sieve 5 Å column is recommended.

**5.2.3    Non-polar WCOT fused silica capillary column,** for the separation of $C_3$ to $C_8$ hydrocarbons.

The separation efficiency of this column is sufficient, if the peak resolution of benzene and cyclohexane meet the performance requirements given in 7.1.

A 50 m $\times$ 0,32 mm i.d., 5 µm phase thickness, methyl silicone capillary column is recommended.

Alternative separation columns may be used if comparable separation efficiency is achieved.

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3)   Porous layer open tubular (PLOT) column filled with Porapak U. Porapak U is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 6974 and does not constitute an endorsement by ISO of this product.
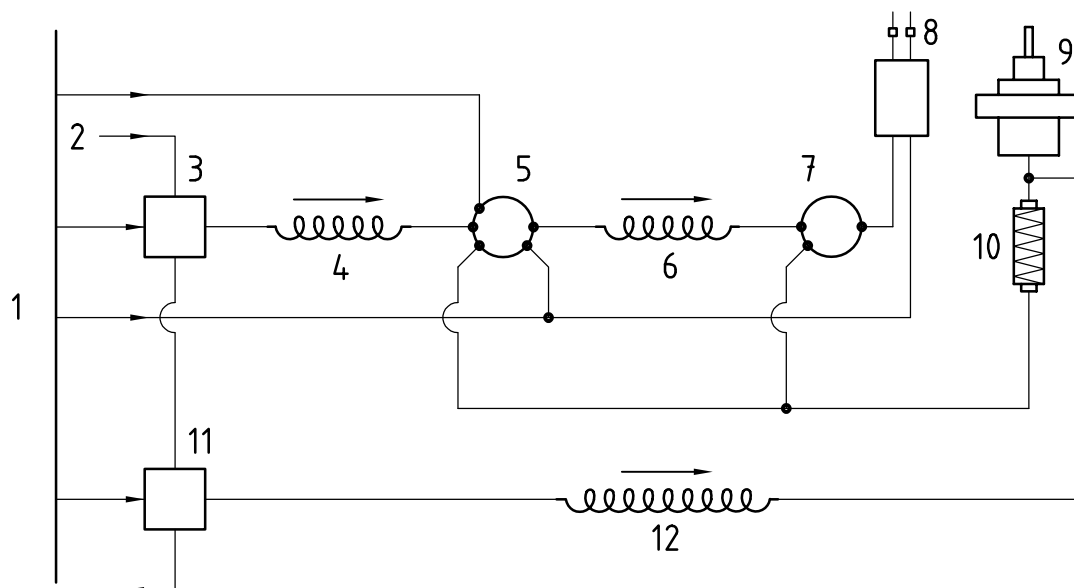
**Key**

1 Carrier gas
2 Sample
3 Gas sample valve 1
4 PLOT precolumn
5 Valve 1
6 Molecular sieve PLOT column
7 Valve 2
8 TCD
9 FID
10 Methanizer
11 Gas sample valve 2
12 WCOT column

**Figure 4 — Flow diagram of a gas chromatograph using a methanizer for CO reduction (8-port micro valve with on-line switching system and methanizer)**
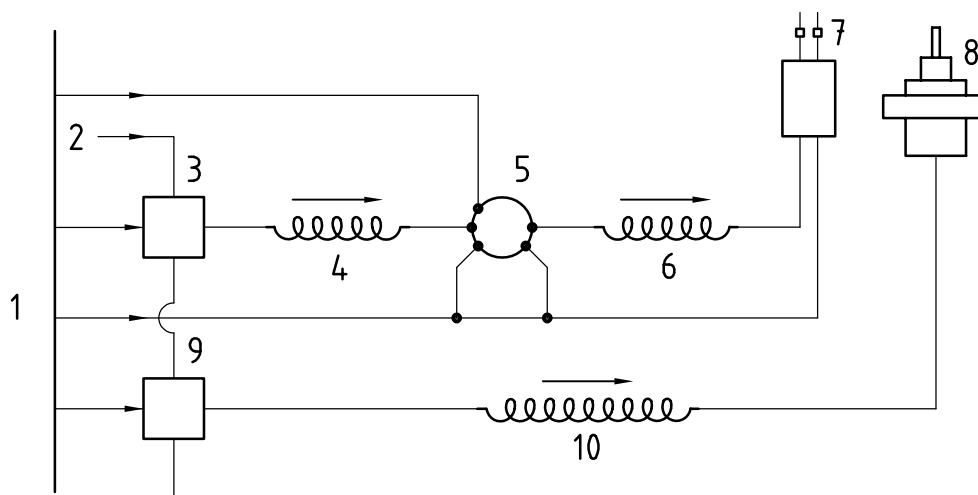
**Key**

1   Carrier gas
2   Sample
3   Gas sample valve 1
4   PLOT precolumn
5   Valve 1
6   Molecular sieve PLOT column
7   TCD
8   FID
9   Gas sample valve 2
10  WCOT column

**Figure 5 — Flow diagram of a gas chromatograph without methanizer
(8-port micro valve with on-line switching system)**

# 6   Procedure

## 6.1   Operating conditions

### 6.1.1   Gas chromatograph

Set up the gas chromatograph (column installation, carrier and auxiliary gas flow rates, oven programmes, detector and injector temperatures, valve switching program) according to the manufacturer's instructions. An example of gas chromatographic conditions is given in Table 3. These conditions are intended to be informative only and may readily be adapted to a particular application.

### 6.1.2   Column conditioning

A molecular sieve strongly adsorbs traces of water, which results in a deteriorated separation. Thus, especially if the separation is performed in an isothermal mode, frequent conditioning of the PLOT columns as specified by the column manufacturer is strongly recommended. If the column oven has temperature gradient capabilities, it is advisable to include a temperature ramp for column conditioning at the end of each run.

This ramp also provides a sharper CO peak when analysing natural gas substitutes.

The maximum operating temperature of Instrument 1 is limited by the manufacturer's specifications of the PoraPLOT precolumn.

**Table 3 — Example of gas chromatographic conditions**

| Gas chromatograph | Instrument 1 | | Instrument 2 |
|---|---|---|---|
| **Columns** | | | |
| Phase | PoraPLOT U[a] | Molecular sieve 5 Å [a] | Methyl silicone |
| Length (m) | 25 | 50 | 50 |
| Internal diameter (mm) | 0,53 | 0,53 | 0,32 |
| Phase Thickness (µm) | 20 | 50 | 5 |
| Maximum temperature (°C) | 190 | 300 | 320 |
| Carrier gas (purity) | Ar (99,999 %) | Ar (99,999 %) | $N_2$ (99,999 %) |
| Flow-rate (ml/min) | 4 | — | 0,6 |
| **Oven programm** | | | |
| Initial temperature (°C) | 30 | | 35 |
| Initial time (min) | 31 | | 12 |
| Ramp rate (°C/min) | 12 | | 8 |
| Final temperature | 120 | | 240 |
| Final time | 10 | | 6 |
| **Detectors** | | | |
| Detector type | TCD | FID | FID |
| Temperature (°C) | 140 | 240 | 280 |
| Make up flow (ml/min) | 1,5 | 0 | 30 |
| to reference cell | 16 | — | — |
| to methanizer | | 35 | — |
| **Injectors** | | | |
| Valve | 0,25 ml | — | 0,25 ml |
| Split flow (ml/min) | 0 | — | 40 |
| **Methanizer** (optional) | — | Nickel catalyst | — |
| Temperature (°C) | — | 375 | — |

[a] The molecular sieve column shall be conditioned separately from the PoraPLOT U column as the conditioning temperatures are different.

### 6.1.3 Sample introduction

Introduce the sample in a defined and reproducible manner into both gas sample valves (see Figure 4). Take care that sample valves and loops are maintained at a constant temperature, at which no condensation of sample components may occur.

Use a purge volume exceeding at least 20 times the volume of the valves, loops and associated gas lines. Insufficient purging of the sample valves and loops results in memory effects from previous samples or in diluting the sample volume with air.

Before injection, bring the samples to ambient pressure.

If a dual oven gas chromatograph is used, delay the switching time of the gas sample valve 2 (see Figure 4) with respect to the switching time of the gas sample valve 1, so as to delay the first peak ($CH_4$) from eluting from the PLOT precolumn. This will prevent the $CH_4$ from masking the other components eluting from the PLOT precolumn,

i.e. $CO_2$, $C_2H_2$, $C_2H_4$ and $C_2H_6$, in the chromatogram. However, make sure this delay does not affect the sample integrity (dilution by air break-in).

Control purge time and sample flow rate during sample introduction.

Controlled pressure equalization may be performed either by waiting for a precisely controlled time after purging or by monitoring the pressure inside the sample loop.

## 6.2 Performance requirements

### 6.2.1 Column performance evaluation

Test the peak resolution as part of the routine analytical cycle.

For each component to be quantified independently, the resolution between neighbouring peaks shall exceed 1,5. Determine the peak resolution as specified in ISO 7504. If the required resolution is not achieved, these particular components shall not be quantified and reported independently.

Typical peak resolution is given in Table 4.

NOTE        The treatment of insufficient peak separation depends on the data processor and the integrator used.

**Table 4 — Typical peak resolution**

| Component 1 | Component 2 | Typical resolution |
|---|---|---|
| Methane ($CH_4$) | Carbon dioxide ($CO_2$) | 18,8 |
| Hydrogen ($H_2$) | Helium (He) | 5,5 |
| Benzene ($C_6H_6$) | Cyclohexane ($C_6H_{12}$) | 5,6 |
| Propene ($C_3H_6$) | Propane ($C_3H_8$) | 0,7 |

### 6.2.2 Relative response factors

Determine the relative response factors as specified in ISO 6974-2.

### 6.2.3 Response characteristics

Determine the response characteristic as specified in ISO 6974-2 at least once a year.

## 6.3 Determination

### 6.3.1 Components He, $H_2$, $O_2$, $N_2$, $CH_4$, CO, $CO_2$, $C_2H_2$, $C_2H_4$ and $C_2H_6$

See Figures 1, 2 and 3 for the column arrangements of Instrument 1 at different stages of the analysis.

Introduce the sample into the PLOT precolumn, where the permanent gases, CO and $CH_4$, have little retention on the precolumn and thus are separated from the $C_2$ and higher hydrocarbons. Transfer the components eluting early, i.e. He, $H_2$, $O_2$, $N_2$, $CH_4$ and CO, to the molecular sieve column for separation. Use the TCD to detect the permanent gases and $CH_4$. To detect CO, eluting last from the molecular sieve column, switch the column in-line to the methanizer-FID arrangement.

Further separate $CO_2$ and the hydrocarbons, not transferred to the molecular sieve column, using the PLOT precolumn, then detect them using the methanizer-FID arrangement. After $C_2H_6$ has been eluted, backflush the $C_{3+}$ fraction to vent. Examples of typical chromatograms are given in Figures 6 and 7.

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Separation may be achieved on both the molecular sieve and the precolumn in an isothermal mode (see 6.5).

Hydrogen and helium may also be determined indirectly although the problem with proper response factor selection for TCD is well recognized. In general, nitrogen ($N_2$) may be used as a reference component.

Since the TCD gives a poor response to carbon monoxide when using argon as a carrier gas, it is advisable to use the FID to determine CO at mole fractions $< 0,2$ %. For this purpose, CO is directed via valve 2 into the methanizer and the FID.

### 6.3.2 Hydrocarbons and higher

Connect the WCOT methyl silicone column directly to its gas sample valve and the FID (see Figure 5). Perform separation using a suitable temperature program (e.g. 35 °C to 240 °C at a rate of 8 °C/min). Use butane as the reference component for the determination of pentanes and higher hydrocarbons.

Adjust the heating rate of the temperature program, so as to separate CO from the other peaks in the FID chromatogram.

### 6.3.3 Detection

#### 6.3.3.1 TCD

Use the TCD for the detection of He, $H_2$, $O_2$, $N_2$ and $CH_4$.

CO can be detected at mole fractions $> 0,2$ % and $CO_2$ at mole fractions $> 0,02$ %.

#### 6.3.3.2 FID

Connect the FID to two columns by means of a fitting.

Use the FID for the detection of $C_2H_2$, $C_2H_4$ and $C_2H_6$ eluting from the PoraPLOT U precolumn and all hydrocarbons above $C_3H_6$ eluting from the WCOT methyl silicone capillary column.

When analysing natural gas substitutes, use the FID also for the detection of $CO_2$ (after reduction to $CH_4$ in the methanizer), $C_2H_2$ and $C_2H_4$ eluting from the PoraPLOT U precolumn and CO (after reduction to $CH_4$ in the methanizer).

Peaks resulting from $CH_4$, $C_2H_2$, $C_2H_4$ and $C_2H_6$, which are only in part separated on the WCOT methyl silicone column, are not suitable for quantification.

### 6.3.4 Data acquisition

Start data acquisition for both detector channels simultaneously at the time of the first injection.
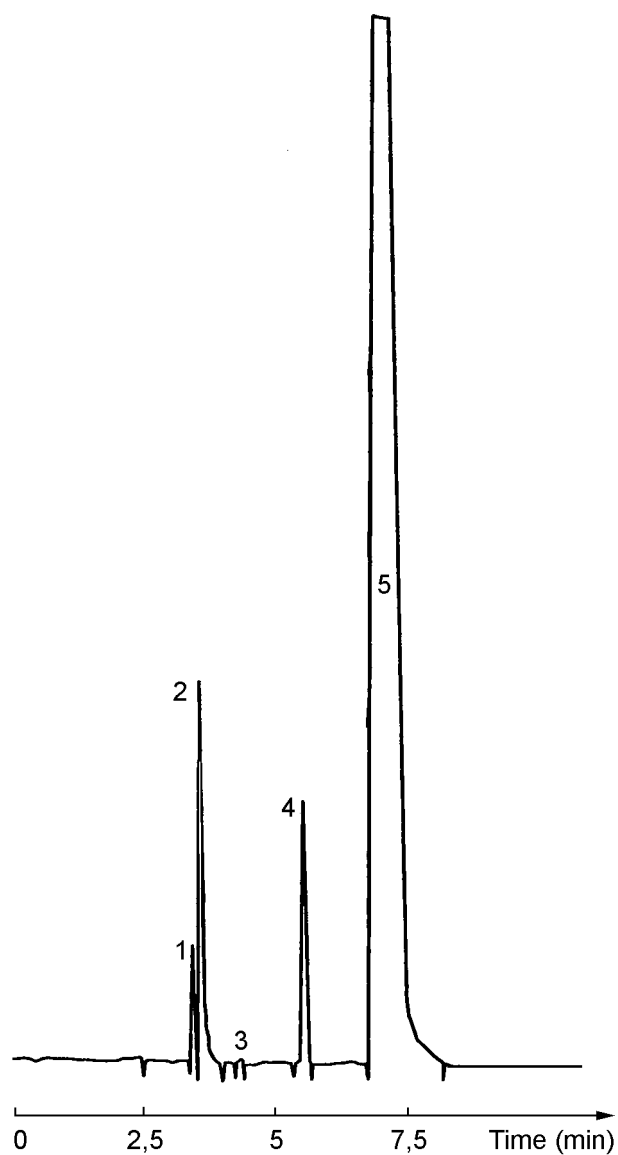
**Key**

1   Helium
2   Hydrogen
3   Oxygen
4   Nitrogen
5   Methane

**Figure 6 — Chromatogram of analysis of helium, hydrogen, oxygen, nitrogen
and methane on the molecular sieve 5Å column**
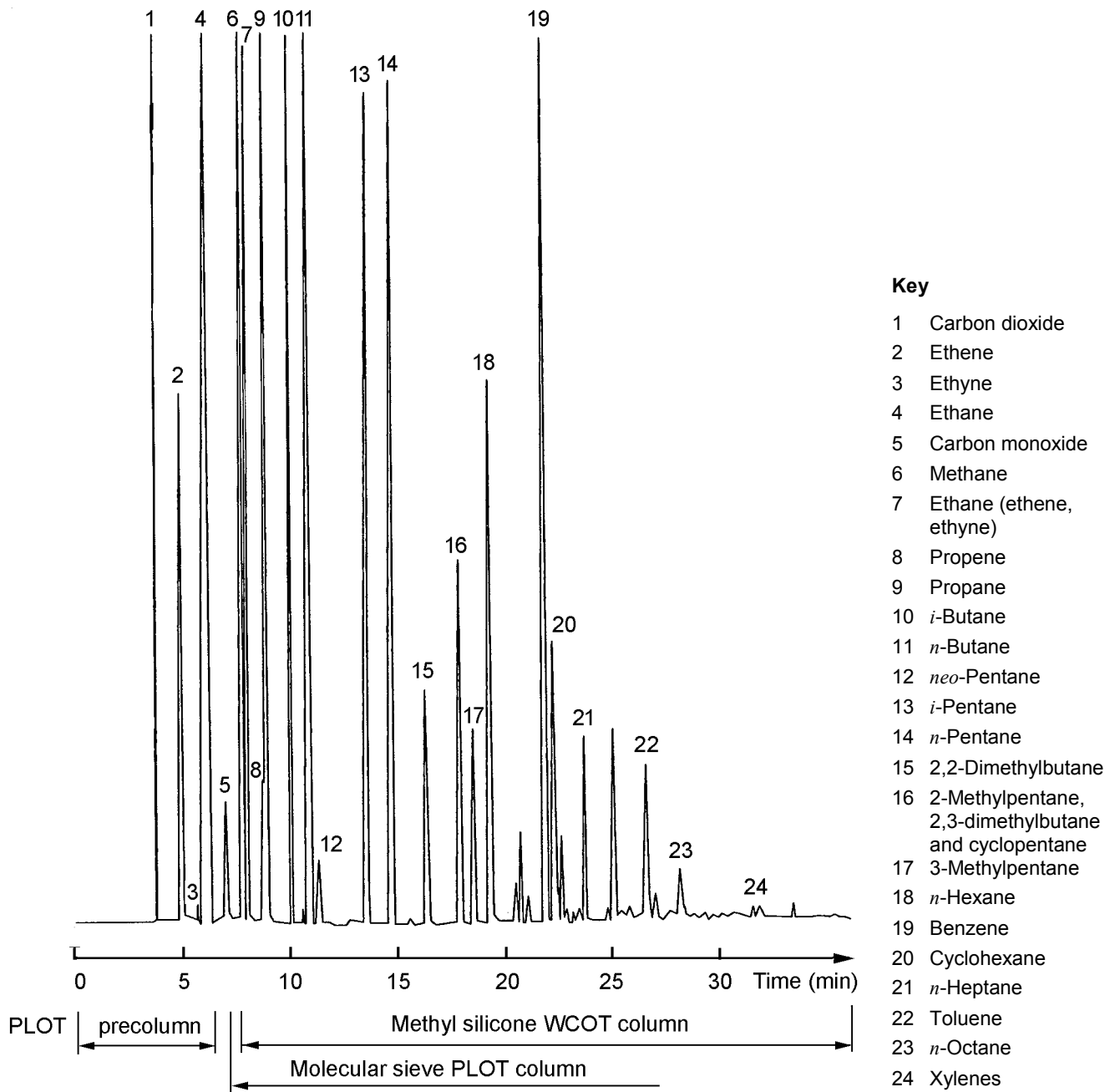
**Figure 7 — Chromatogram of analysis of $CO_2$ and $C_1$ to $C_8$ components on the PoraPLOT U, WCOT and molecular sieve columns**

## 7   Calculation

Calculate the mole fractions of the components in accordance with ISO 6974-1.

## 8   Precision

Typical values for precision that may be achieved with this method are given in annex A.

## 9   Test report

Report the results in accordance with clause 14 of ISO 6974-1:2000.

# Annex A
## (informative)

# Typical precision values

Typical precision values are given in Table A.1. These values have been obtained from practical experience and give an indication of the performance of the method. As such, they cannot be compared with precision values mentioned in informative annexes of other parts of ISO 6974, as they are very much dependent on the quality of the calibration gases used and the laboratory skills.

**Table A.1 — Repeatability and reproducibility of measurement results**

| Sample $x$ concentration range mole fraction (%) | Repeatability | | Reproducibility | |
|---|---|---|---|---|
| | Absolute mole fraction (%) | Relative % | Absolute mole fraction (%) | Relative % |
| $x < 0,1$ | 0,002 | — | 0,002 | — |
| $0,1 < x \leqslant 1$ | — | 2 | — | 4 |
| $1 < x \leqslant 50$ | — | 0,8 | — | 1,6 |
| $50 < x \leqslant 100$ | — | 0,08 | — | 0,16 |

# Bibliography

[1] ISO 6974-3, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to $C_8$ using two packed columns*

[2] ISO 6974-4, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and $C_1$ to $C_5$ and $C_{6+}$ hydrocarbons for a laboratory and on-line measuring system using two columns*

[3] ISO 6974-5, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and $C_1$ to $C_5$ and $C_{6+}$ hydrocarbons for a laboratory and on-line process application using three columns*

[4] ISO 6976, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition*

[5] ISO 10715, *Natural gas — Sampling guidelines*

[6] ISO 10723 *Natural gas — Performance evaluation for on-line analytical systems*

**ISO 6974-6:2002(E)**