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

Part 6:

**Determination of hydrogen, helium,
oxygen, nitrogen, carbon dioxide and
C₁ to C₈ 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 (C₁ à C₈) 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 C₈ using two packed columns*
- *Part 4: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line measuring system using two columns*
- *Part 5: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line process application using three columns*
- *Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C₁ to C₈ 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.

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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 C₁ to C₈ 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 C₁ to C₈ 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 ₂ H ₂	0,001	to	0,5
Ethene ^a	C ₂ H ₄	0,001	to	0,5
Ethane	C ₂ H ₆	0,002	to	15
Propene ^{a b}	C ₃ H ₆	0,001	to	0,5
Propane ^b	C ₃ H ₈	0,001	to	5
<i>i</i> -Butane	C ₄ H ₁₀	0,000 1	to	1
<i>n</i> -Butane	C ₄ H ₁₀	0,000 1	to	1
2,2-Dimethylpropane (Neopentane)	C ₅ H ₁₂	0,000 1	to	0,5
2-Methylbutane (<i>i</i> -Pentane)	C ₅ H ₁₂	0,000 1	to	0,5
<i>n</i> -Pentane	C ₅ H ₁₂	0,000 1	to	0,5
Cyclopentane	C ₅ H ₁₀	0,000 1	to	0,5
2,2-Dimethylbutane	C ₆ H ₁₄	0,000 1	to	0,5
2,3-Dimethylbutane	C ₆ H ₁₄	0,000 1	to	0,5
2-Methylpentane	C ₆ H ₁₄	0,000 1	to	0,5
3-Methylpentane	C ₆ H ₁₄	0,000 1	to	0,5
<i>n</i> -Hexane	C ₆ H ₁₄	0,000 1	to	0,5
Benzene	C ₆ H ₆	0,000 1	to	0,5
Cyclohexane	C ₆ H ₁₂	0,000 1	to	0,5
Heptanes ^c	C ₇ H ₁₆	0,000 1	to	0,5
Methylcyclohexane	C ₇ H ₁₄	0,000 1	to	0,5
Toluene	C ₇ H ₈	0,000 1	to	0,5
Octanes ^d	C ₈ H ₁₈	0,000 1	to	0,5
Xylenes ^e	C ₈ H 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: <i>n</i> -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: <i>n</i> -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>i</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: <i>o</i> -xylene, <i>m</i> -xylene, <i>p</i> -xylene. <i>m</i> - and <i>p</i> -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 PLOT¹⁾ 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 WCOT²⁾ 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), $\geq 99,999$ % pure, free from oxygen and water.

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

4.2 Auxiliary gases

4.2.1 For FID detection:

4.2.1.1 Nitrogen (N_2) or helium (He), $\geq 99,996$ % 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), $\geq 99,999$ % pure, free from corrosive gases and organic compounds.

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

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

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 mole fraction (%)	WRM 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 CH₄, CO and CO₂ 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:

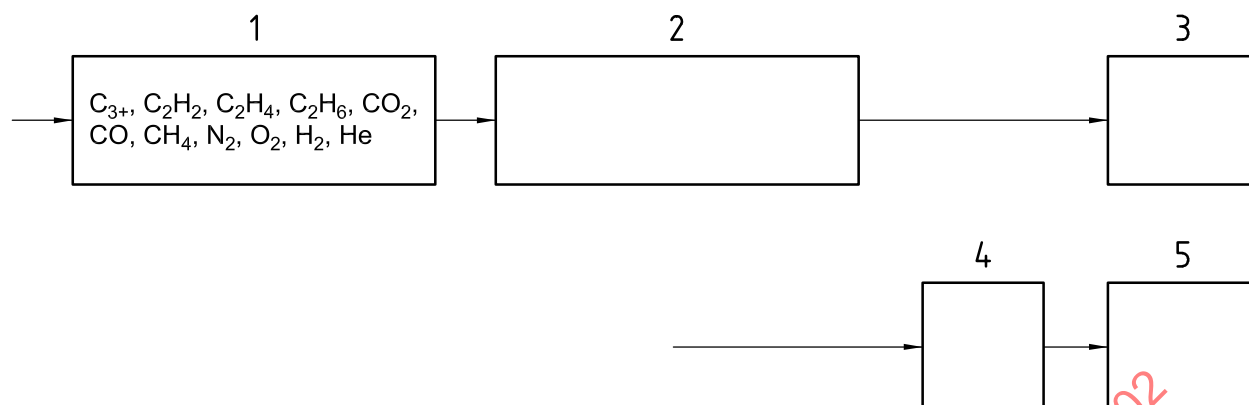
5.1.1 Two column ovens, for temperature-programmed operation, capable of following a given linear temperature gradient (see Table 3).

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).

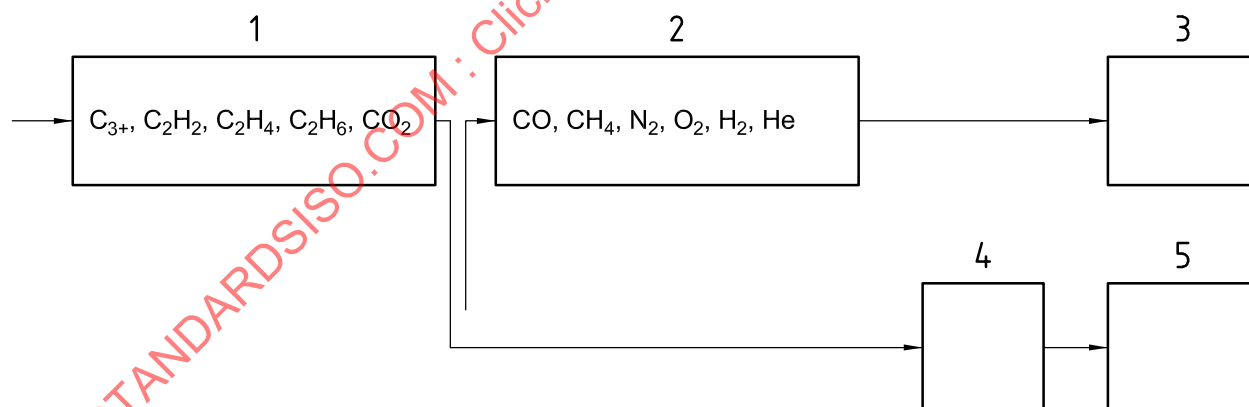
Instrument 1 may alternatively be equipped with a column oven for isothermal operation for a temperature range from 40 °C to 140 °C and capable of maintaining the temperature to within $\pm 0,1$ °C at any point inside the oven chamber.

5.1.1.2 Instrument 2 oven, containing the WCOT column.

**Key**

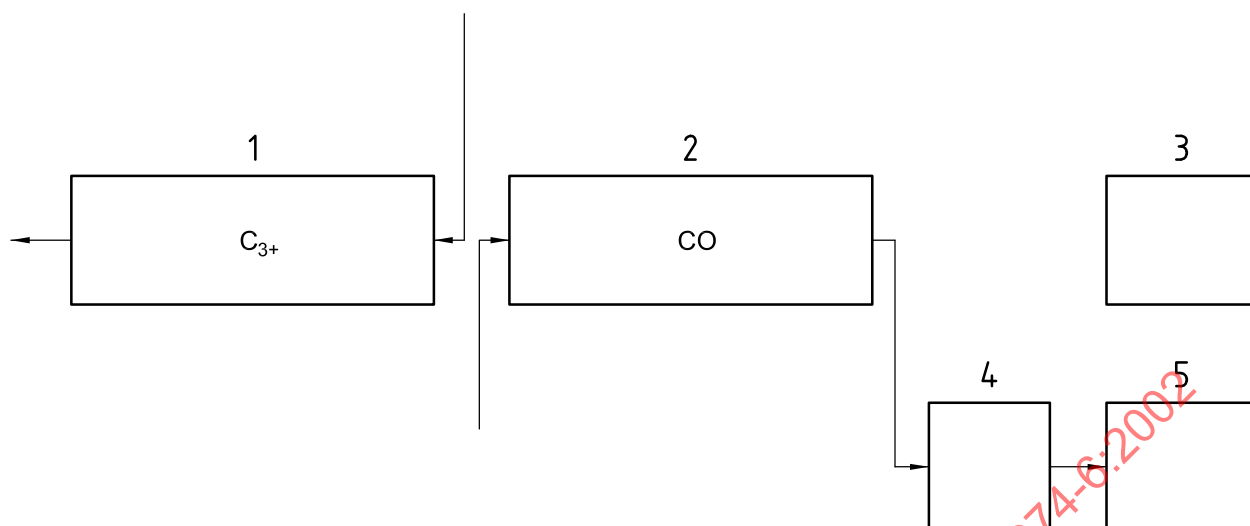
- 1 Plot precolumn
- 2 Molecular sieve Plot column
- 3 TCD
- 4 Methanizer
- 5 FID

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 CO₂ and C₂

**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 C₃₊ 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 (CO₂) to CH₄ 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 U³⁾ 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.

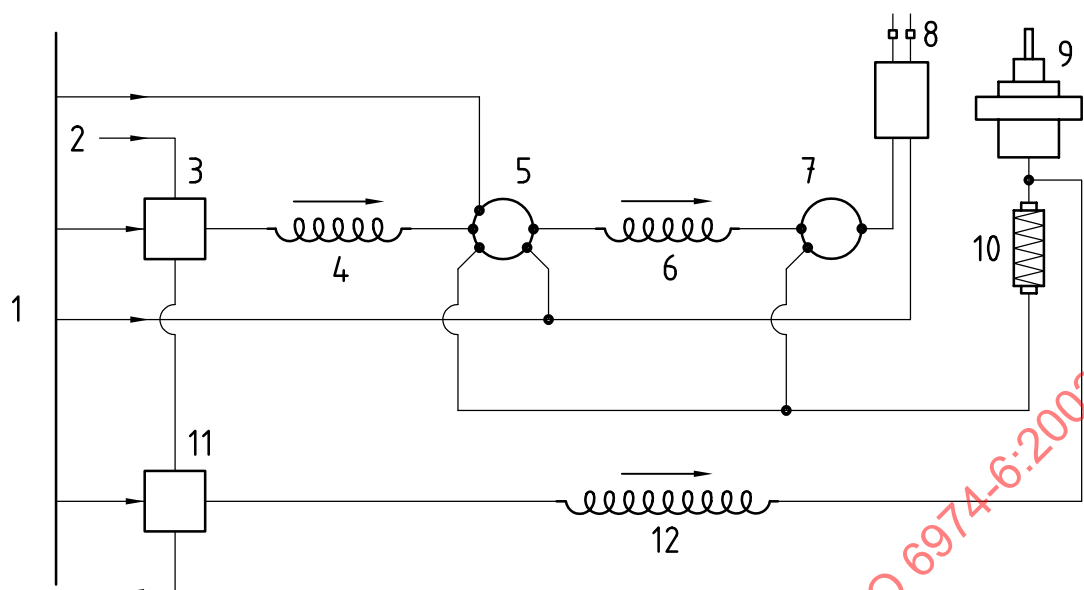
5.2.3 Non-polar WCOT fused silica capillary column, for the separation of C_3 to C_8 hydrocarbons.

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.

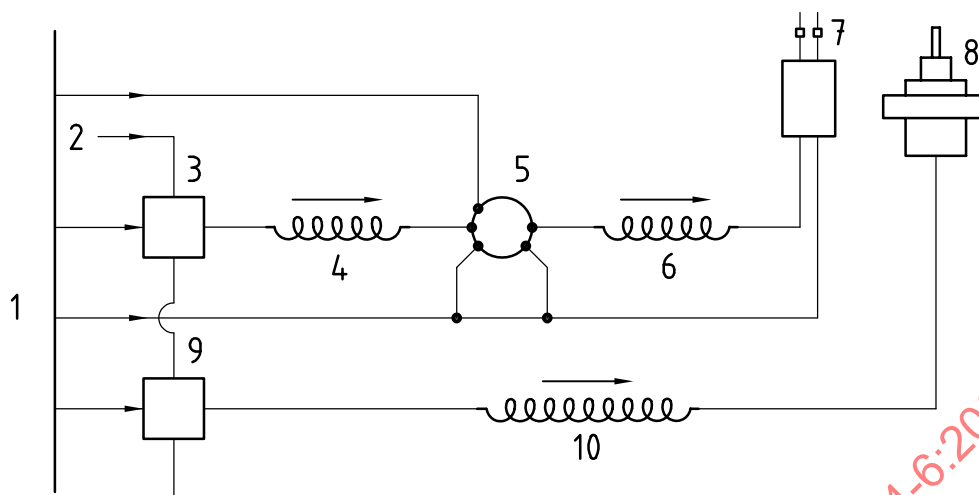
3) Porous layer open tubular (PLOT) column filled with Porapak U. Porapak U is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 6974 and does not constitute an endorsement by ISO of this product.



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 (CH₄) from eluting from the PLOT precolumn. This will prevent the CH₄ from masking the other components eluting from the PLOT precolumn,

i.e. CO₂, C₂H₂, C₂H₄ and C₂H₆, 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 ₆ H ₆)	Cyclohexane (C ₆ H ₁₂)	5,6
Propene (C ₃ H ₆)	Propane (C ₃ H 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, H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₂, C₂H₄ and C₂H₆

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 CH₄, have little retention on the precolumn and thus are separated from the C₂ and higher hydrocarbons. Transfer the components eluting early, i.e. He, H₂, O₂, N₂, CH₄ and CO, to the molecular sieve column for separation. Use the TCD to detect the permanent gases and CH₄. To detect CO, eluting last from the molecular sieve column, switch the column in-line to the methanizer-FID arrangement.

Further separate CO₂ and the hydrocarbons, not transferred to the molecular sieve column, using the PLOT precolumn, then detect them using the methanizer-FID arrangement. After C₂H₆ has been eluted, backflush the C₃₊ fraction to vent. Examples of typical chromatograms are given in Figures 6 and 7.

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. $35\text{ }^{\circ}\text{C}$ to $240\text{ }^{\circ}\text{C}$ at a rate of $8\text{ }^{\circ}\text{C}/\text{min}$). 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.

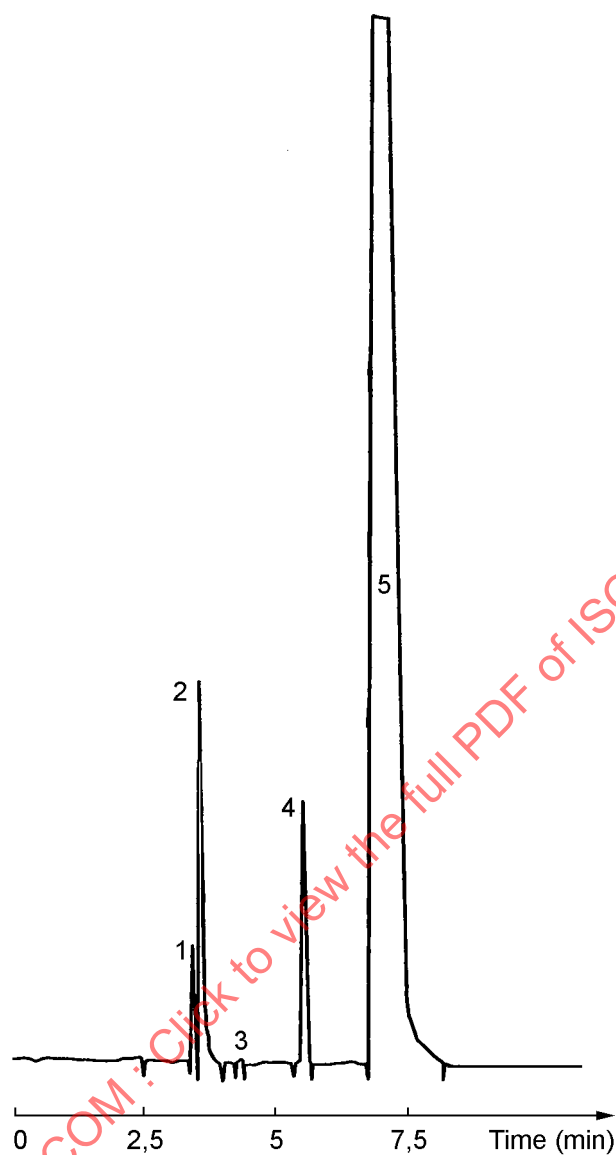
Use the FID for the detection of C_2H_2 , C_2H_4 and C_2H_6 eluting from the PoraPLOT U precolumn and all hydrocarbons above C_3H_6 eluting from the WCOT methyl silicone capillary column.

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 5A column