# INTERNATIONAL STANDARD

# ISO
# 6974-5

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

## 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

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

*Partie 5: Détermination de l'azote, du dioxyde de carbone et des hydrocarbures (C1 à C5 et C6+) pour l'application du processus en continu employant trois colonnes*

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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.

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.

International Standard ISO 6974-5 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This part as well as the other five parts of ISO 6974 cancel and replace 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 data treatment*

— *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 hydrocarbons up to $C_8$ using three capillary columns*

Annexes A and B of this part of ISO 6974 are for information only.

# Introduction

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

This method is based on a automatic column-switching technique in which multiple columns, chosen for their separating ability for particular groups of components, are switched automatically.

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 5:
Determination of nitrogen, carbon dioxide and hydrocarbons C1 up to C5 and C6+ for a laboratory and on-line process application using three columns

## 1 Scope

This part of ISO 6974 describes a gas chromatographic method for the quantitative determination of natural gas constituents using a three-column system. This method is applicable to natural gases of limited range, on-line and automatically calibrating on a regular basis for gas samples not containing any hydrocarbon condensate and/or water. It is applicable to the analysis of gases containing constituents within the mole fraction ranges given in Table 1. 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 detected present, 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.

**Table 1 — Application ranges**

| Component | Mole fraction range % |
|---|---|
| Nitrogen | 0,001 to 15,0 |
| Carbon dioxide | 0,001 to 8,5 |
| Methane | 75 to 100 |
| Ethane | 0,001 to 10,0 |
| Propane | 0,001 to 3,0 |
| *iso*-Butane (2-methylpropane) | 0,001 to 1,0 |
| *n*-Butane | 0,001 to 1,0 |
| *neo*-Pentane (2,2-dimethylpropane) | 0,001 to 0,5 |
| *iso*-Pentane (2-methylbutane) | 0,001 to 0,5 |
| *n*-Pentane | 0,001 to 0,5 |
| Hexanes + sum of all $C_6$ and higher hydrocarbons | 0,001 to 1,0 |

NOTE 1   Hydrocarbons higher than *n*-pentane are expressed as the "pseudo-component" $C_{6+}$ which is measured as one composite peak and calibrated as such. The properties of $C_{6+}$ are calculated from detailed analyses of the individual $C_6$ and higher hydrocarbons by extended analysis or from historical data.

NOTE 2   Oxygen is not a normal constituent of natural gas and would not be expected to be present in gas sampled for an on-line instrument. If any oxygen is present as a result of air contamination, it will be measured with the nitrogen. The resulting (nitrogen + oxygen) value will be in error to a small extent because of the slight difference between detector responses for

oxygen and nitrogen. Nonetheless, the result for the natural gas/air mixture will be reasonably accurate since neither component contributes to the calorific value.

NOTE 3    The content of helium and argon are assumed to be negligible and unvarying such that helium and argon need not be determined.

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

ISO 6974-2:—[1]), *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for data treatment.*

ISO 7504:1984, *Gas analysis — Vocabulary.*

# 3   Principle

Determination of nitrogen, carbon dioxide and hydrocarbons from $C_1$ to $C_{6+}$ by gas chromatography using a three-column switching/backflush arrangement, configured as shown in Figure 1. The three chromatographic columns are connected by two six-port valves for handling sample injection and backflushing operations (or alternatively a single ten-port valve is used) to a thermal conductivity detector (TCD) which is used for quantification.

A single sample is injected first onto a boiling-point separation column, divided into short and long sections. The $C_6$ and heavier hydrocarbons are initially retained on the short section of this column. The long section of this column retains $C_3$ to $C_5$ hydrocarbons. The lighter components (nitrogen, methane, carbon dioxide and ethane) pass rapidly and unresolved through the boiling-point separation column onto a porous polymer-bead column, suitable for their retention and separation. Following an accelerated backflush of the short column situated closest to the detector, the heavier $C_{6+}$ hydrocarbons (determined as a recombined "pseudo component" rather than by the summation of individual component measurements) elute first and are quantified as a single peak. Next, from the longer section of this column situated farther from the detector, the $C_3$ to $C_5$ hydrocarbons are separated then quantified by TCD. Finally, by redirecting carrier gas onto the porous polymer-bead column, the lighter components, i.e. nitrogen, carbon dioxide, methane and ethane, are separated then quantified by the detector. A six-port valve either connects this column to the carrier-gas flow or by-passes it during measurement of $C_3$ to $C_5$ components.

The separations that occur in the columns are as follows:

Column 1    Retains $C_{6+}$ components ready for backflushing as one composite peak.

Column 2    Separates propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane and *n*-pentane, (which elute after $C_{6+}$ has left column 1).

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1)    To be published.

Column 3   Retains and separates nitrogen, methane, carbon dioxide and ethane which elute after *n*-pentane has left column 2.

## 4   Materials

**4.1   Helium carrier gas**, > 99,99 % pure, free from oxygen and water.

**4.2   2-Dimethyl-butane**, used to check complete backflushing of $C_{6+}$, 95% pure.

**4.3   Working-reference gas mixtures** (WRM), the composition of which shall be chosen to be similar to that of the anticipated sample.

A cylinder of distributed natural gas, containing all the components measured by this method is to be used by the laboratory as a control gas. The working-reference gas mixtures shall be prepared in accordance with ISO 6142. The working-reference gas mixture shall contain at least nitrogen, carbon dioxide, methane, ethane, propane, *n*-butane, *iso*-butane and possibly *iso*-pentane, *n*-pentane, *neo*-pentane and *n*-hexane.

## 5   Apparatus

**5.1   Laboratory gas chromatographic** (GC) **system,** consisting of the following components:

**5.1.1   Gas chromatograph** (GC), capable of isothermal operation and equipped as follows:

a)   **column oven**, capable of being maintained to within $\pm$ 0,1 °C over the temperature range: 70 °C to 105 °C;

b)   **valve oven**, capable of being maintained over the temperature range 70 °C to 105 °C or alternatively having the capacity to fit the valves in the column oven;

c)   **flow regulators**, capable of regulating the carrier gas flowrates.

**5.1.2   Injection device,** consisting of a ten-port sample-injection valve V1 and also used for backflushing $C_{6+}$ components (two six-port valves may be used for these duties using the same operating principle). See Figure 1.

**5.1.3   Column isolation valve,** six-port, to by-pass the porous polymer bead column (column 3). See valve 2 in Figure 1.

**5.1.4   Metal columns packed with either 28 % DC-200/500 on Chromosorb PAW or 15 % DC-200/500 on Porapak N,** satisfying the performance requirements given in clause 6.3 and consisting of the following packing materials and column dimensions, given as examples, for use with conventional and readily available injection valves and TCD.

Any alternative combination of columns which provide similar separations and satisfy the performance requirements may be used. Micro-packed or even capillary columns can be chosen, with appropriately-sized injection and detector systems, in which case packing or coating details would be different.

Columns shall satisfy the following requirements:

a)   metal tubing:

   —   column 1: 0,75 m (2,5 ft) long, 2 mm internal diameter (i.d.) (1/8 in o.d.)

   —   column 2: 5,2 m (17 ft) long, 2 mm i.d. (1/8 in o.d.)

   —   column 3: 2,4 m (8 ft) long, 2 mm i.d. (1/8 in o.d.)

b)   packing:

— column 1: 28 % DC-200/500 on Chromosorb PAW (45 ASTM mesh to 60 ASTM mesh)

— column 2: 28 % DC-200/500 on Chromosorb PAW (45 ASTM mesh to 60 ASTM mesh)

— column 3: 15 % DC-200/500 on Porapak N (50 ASTM mesh to 80 ASTM mesh) for the separation of nitrogen, methane, carbon dioxide and ethane

NOTE    Columns 1 and 2 are boiling-point separation columns for the separation of propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane. They effectively are a single column, divided into short and long sections for rapid backflush of $C_{6+}$ components to the detector.

c)  method of packing: packed by any suitable packing method providing uniform column packing and performance characteristics in accordance with 6.2. If purchased individually, as part of a system, or packed individually, their performance shall comply with the specification. When packed individually it is assumed that this will be according to a recognized technique.

NOTE    The following packing method is suitable:

Close the column outlet with a sintered disc or glass wool plug. Connect a reservoir containing rather more packing than is needed to fill the column to the inlet and apply a pressure of 0,4 MPa of nitrogen to this reservoir. The flow of packing into the column is assisted by vibration. When the column is full, allow the pressure to decay slowly before disconnecting the reservoir.

d)  conditioning: with freshly prepared columns, more stable baselines can be obtained by conditioning them overnight, with carrier gas flowing, at a temperature of 50 °C higher than that at which they are intended to operate. If this is necessary, but not easily achieved in the gas chromatograph in which the columns are to be used, they can be conditioned after being installed in another unit.

**5.1.5    Thermal conductivity detector** (TCD), with a time constant of not greater than 0,1 s, and internal volume appropriate for the column sizes and flowrate used.

**5.1.6    Controller/peak-measurement system**, having a wide range of sensitivity (0 V to 1 V), capable of measuring peaks on a sloping baseline and able to control automatic operation of the valves according to a sequence selected by the operator.

**5.1.7    Auxiliary equipment**, consisting of valves, tubing and any other accessories, to control the flow of sample gas to the chromatograph and for shutting off this flow for a defined period of time before injection.

# 6   Procedure

## 6.1   Gas chromatographic operating conditions

If the apparatus has been used for previous determinations, ensure that it is returned to the starting conditions before injecting a sample or calibration gas mixture.

Set the operating conditions for the apparatus (5.1) as follows.

a)  Oven column: 70 °C to 105 °C, capable of being maintained to within ± 0,1 °C

b)  Carrier gas flowrate: dependent upon the column diameter. With the carrier gas flowing through all columns in the order column 1 to column 2 to column 3 [Figure 1 b)], set the flowrate so that the average linear velocity for nitrogen (total column length divided by hold-up time) is between 10 cm/s and 15 cm/s.

c)  Valves: if the valves are not fitted in the column oven, set them to a temperature in the range of 70 °C to 105 °C (no less than the column temperature), isothermal and stable to ± 2 °C.

d) Detector: TCD

— temperature setting: between 70 °C and 105 °C;

— set the bridge current according to manufacturer's instructions.

e) Controller/peak-measurement system: set up in accordance with the manufacturer's instructions.

Set up the gas chromatograph according to the manufacturer's instructions.

Table 2 summarizes column data and operating conditions for typical implementation of this method.

**Table 2 — Typical chromatographic conditions**

| Column characteristics | Column 1 | Column 2 | Column 3 |
|---|---|---|---|
| Stationary phase | Silicone oil DC-200/500 | Silicone Oil DC-200/500 | Silicone oil DC-200/500 |
| Loading % | 28 % | 28 % | 15 % |
| Support | Chromosorb PAW | Chromosorb PAW | — |
| Active solid | — | — | Porapak N |
| ASTM mesh size | 45/60 | 45/60 | 50/80 |
| Column length | 0,75 m | 5,2 m | 2,4 m |
| Column i.d. | 2 mm | 2 mm | 2 mm |
| Material | Stainless steel | | |
| **Gas chromatographic conditions** | | | |
| Oven temperature | 100 °C | | |
| Carrier gas | Helium | | |
| Pressure | 400 kPa (4 bar) | | |
| Flow | 28 ml/min | | |
| Detector | TCD | | |
| Detector temperature | 100 °C | | |
| Injection device | Valve | | |
| Injection device temperature | 100 °C | | |
| Sample volume | 1,0 ml | | |

## 6.2 Calibration

Calibrate the equipment in accordance with the procedures described in parts 1 and 2 of ISO 6974.

The use of a single calibration standard is consistent either with the assumption that instrument response to a component is represented by a straight line through the origin or that it is some other function which has been well defined. If the response differs from that which is assumed then the use of a single calibration standard will introduce an error. The scale of such an error can be assessed by testing the linearity using the method given in ISO 10723[1] with the wide-ranging test gases prepared as described in ISO 6142. The nature of such testing is outside the scope of this International Standard.

## 6.3    Performance requirements

### 6.3.1    Peak resolution

It is important that all components be measured with as less interference from others as possible. Possible interference can be assessed by measuring peak resolution in accordance with 3.3.4.2 of ISO 7504:1984. Although the resolution of all peaks is important, there are no particular pairs of peaks which are critical although satisfactory resolution of one pair can ensure that of other pairs of peaks.

Furthermore, the resolution required is likely to vary with respect to component uncertainty although it may be deemed acceptable for particular applications. If the procedure is implemented correctly, the acceptable resolution values indicated in Table 3 are to be expected. Higher resolution may require modification of column dimensions, temperature and flowrate, and would likely require longer analysis time.

Each value of resolution shall be tested as part of the normal analytical cycle, not by some alternative procedure designed only to measure these parameters.

**Table 3 — Peak resolution**

| Component 1 | Component 2 | Acceptable resolution | High resolution |
|---|---|---|---|
| *iso*-Butane | *n*-Butane | 1,0 | 1,5 |
| Nitrogen | Methane | 0,75 | 1,5 |
| Carbon dioxide | Ethane | 2,0 | 2,3 |

### 6.3.2    Chromatogram

A typical chromatogram is shown in Figure 2.

The order of elution of components should not change, but actual retention times shall be determined for each individual system.

Measure the areas or heights of component peaks from the detector with an integrator or data system. (Use areas for all major components, but it may be found that peak heights give better repeatability for some minor components, such as the pentanes, where peaks are both small and relatively wide.) Set the integration parameters so as to correctly allocate baselines, and so that there is no interference with peak measurement from valve-switching disturbances.

## 6.4    Determination

### 6.4.1    Sample valve purge

Purge the sample valve with the gas to be analysed, using at least 20 times the volume of the valve and associated pipework.

Stop the purge to enable the gas to reach the temperature of the valve and ambient pressure, then start the analytical cycle, injecting the sample and switching the valves as required.

If this volume of sample is not enough to purge the valve, contamination by air or by the previous sample will interfere with the determination. If either occur, then use a larger volume of sample for purging.

NOTE      The sample loop should be purged with gas for a precise time period, at a defined rate, and the sample should then be allowed to equilibrate to ambient pressure before injection. In the absence of equipment which can confirm the latter, there should be a defined time between sample-valve shut-off and injection.

**6.4.2   Analysis**

The analytical system shown in Figure 1 comprises one ten-port sample-injection/backflush valve, V1, and one six-port by-pass valve V2. Restrictor A maintains the pneumatic balance of the system when column 3 is isolated. The detailed setting-up procedure is given in annex A. (Two six-port valves may be used in place of the 10-port valve V1, one for controlling sample injection and the other backflushing column 1. If these operations are simultaneous, their timings may be taken to be the same as those for a single 10-port valve.)

The time settings of the valve switching operations shall ensure that

a)   V1 is returned to the backflush configuration (configuration 1) after all the *n*-pentane leaves column 1 but before the lowest $C_6$ isomer leaves column 1 on its way to column 2,

b)   V2 is switched to isolate column 3 (configuration 2) before any propane leaves column 2 (on its way to column 3) and after all the ethane has left column 2 and entered column 3,

c)   V2 is not returned to reconnect column 3 (configuration 1) until all the *n*-pentane has been detected, having emerged from column 2 via column 1.
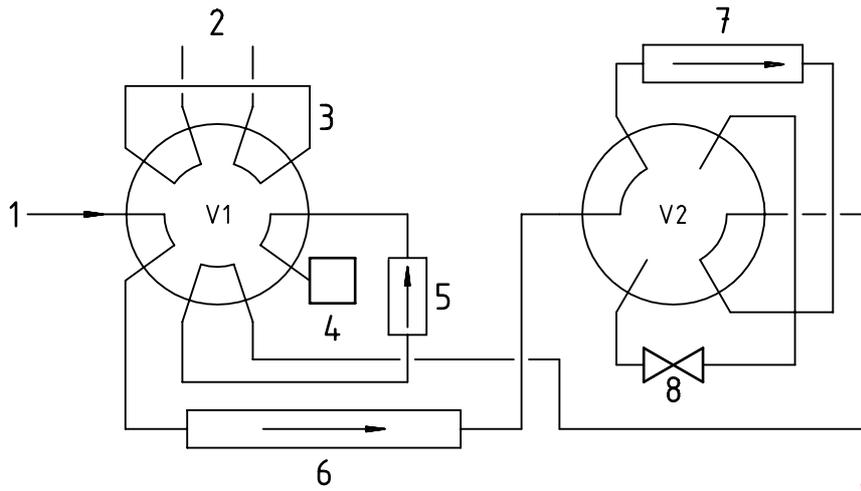
# 7   Expression of results

Refer to ISO 6974-1.
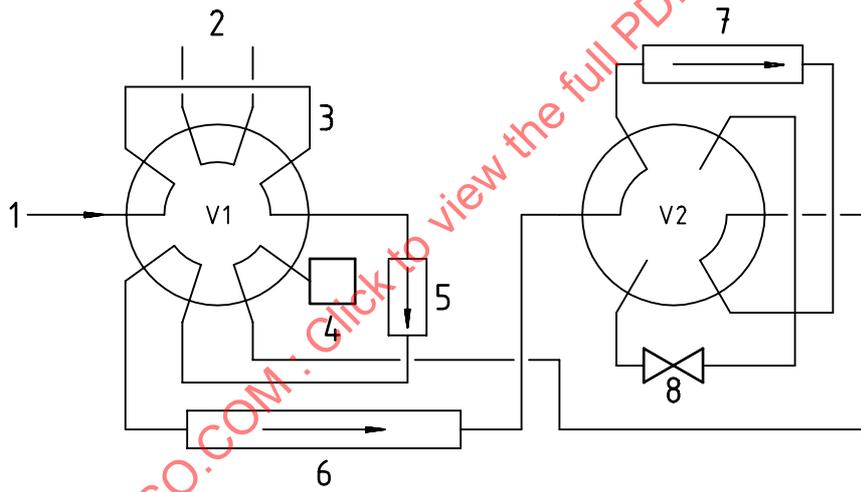
## 7.1   Precision and accuracy

Refer to ISO 6974-2.

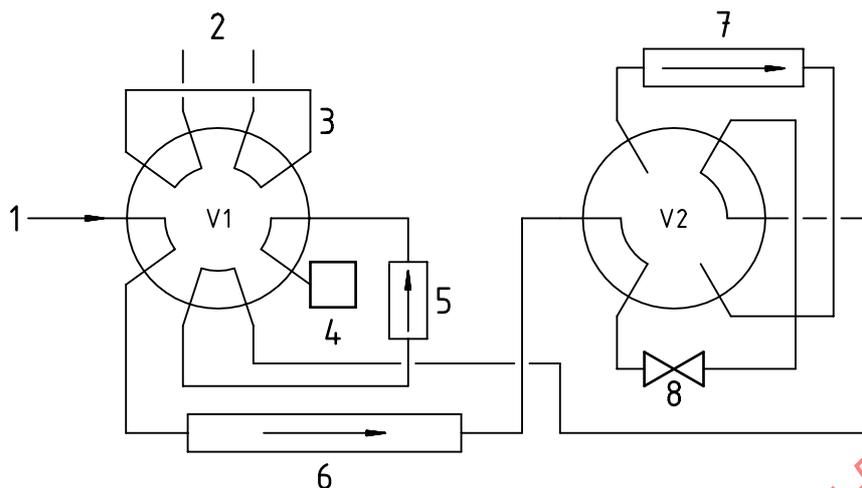See annex B for typical precision values.

# 8   Test report

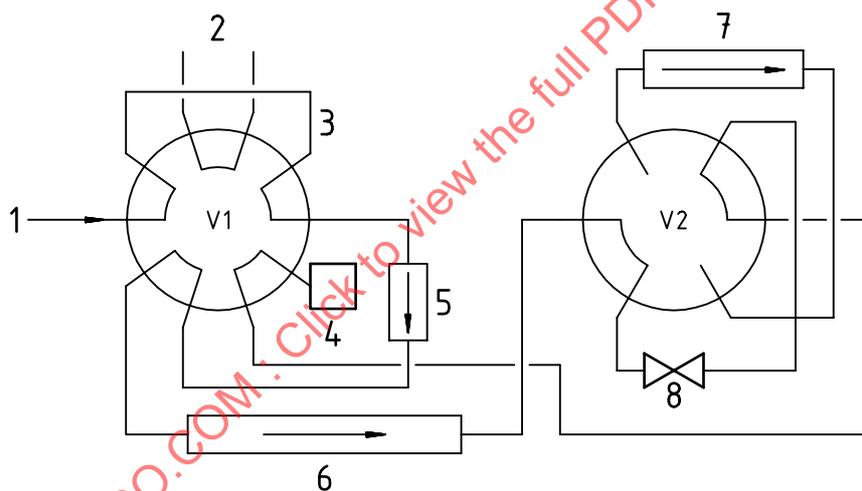Report the results in accordance with clause 14 of ISO 6974-1:2000.

**a) Valve 1 (V1) in configuration 1 and valve 2 (V2) in configuration 1**



**b) Valve 1 (V1) in configuration 2 and valve 2 (V2) in configuration 1**

**c) Valve 1 (V1) in configuration 1 and valve 2 (V2) in configuration 2**



**d) Valve 1 (V1) in configuration 2 and valve 2 (V2) in configuration 2**

**Key**

| | | | |
|---|---|---|---|
| 1 | Carrier gas | 5 | Column 1 |
| 2 | Sample introduction | 6 | Column 2 |
| 3 | Sample loop | 7 | Column 3 |
| 4 | TCD detector | 8 | Restrictor A |

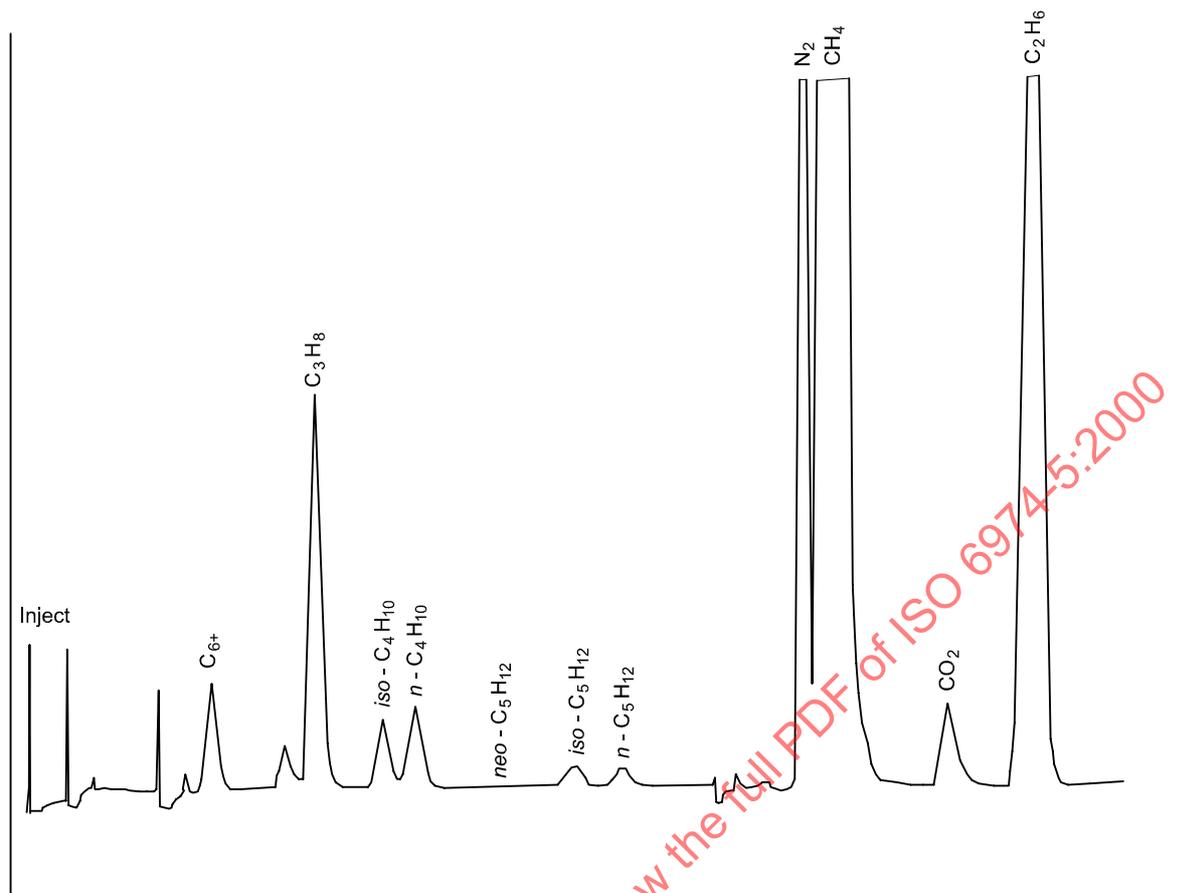**Figure 1 — Valve configurations for natural gas analyser**

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**Figure 2 — Example of a typical chromatogram**

# Annex A
(informative)

# Procedure for setting valve timings and restrictor setting

**A.1**    Set all the valves to configuration 1 [Figure 1 a)], so that the carrier gas flows from column 2 (long boiling-point separation column) to column 3 (porous polymer-bead column) to column 1 (short boiling-point separation column) to the detector. Set the column temperature and the TCD analytical gas-flowrate to manufacturer's suggested values. In the absence of manufacturer's values, use 95 °C and 28 ml/min, for a system using 2 mm i.d. columns.

**A.2**    Switch valve 2 to configuration 2 [Figure 1 c)] to by-pass column 3. Allow the carrier flow to stabilize and then adjust restrictor A so that the TCD analytical flowrate is identical to that measured in A.1.

**A.3**    Set the TCD reference flowrate to the value measured in A.1.

**A.4**    With valve 2 in configuration 2, inject a sample of natural gas by switching valve 1 to configuration 2 [Figure 1 d)]. Record the chromatogram as components elute from column 2. Ensure that the retention time for $n$-pentane is about two-thirds of the anticipated analysis cycle time. If it is significantly different, repeat A.1 after adjusting the flow accordingly. Then repeat A.2 to A.4.

**A.5**    If no switching time is provided by the manufacturer, measure the time from injection to the peak valley minimum between ethane and propane ($t_{first,cut}$). This will be the initial time used for retaining the lighter components on column 3.

**A.6**    Backflushing:

**A.6.1**    The backflush operation allows all of the latest-eluting $C_5$ ($n$-$C_5$) to be measured by forward elution and all of the lightest $C_6$ (2,2-dimethyl butane) to be backflushed. Use a gas mixture containing $n$-$C_5$ and 2,2-dimethyl butane with no other $C_6$ or heavier components present.

**A.6.2**    Set an initial time of 1 min (or as recommended by the manufacturer) after injection at which time valve V1 returns to configuration 1. Switch V2 to configuration 2. Inject the gas mixture and record the chromatogram.

2,2-Dimethyl butane should appear as a backflushed component ($C_{6+}$) shortly after valve V1 returns to configuration 1, and $n$-$C_5$ should appear as a normally eluted peak with a slightly longer retention time than that measured in A.4. (It has to travel through column 1 twice). If no $C_{6+}$ peak is seen, reduce the initial time setting and repeat the operations described in this subclause.

**A.6.3**    Continue to inject the gas mixture, increasing the backflush time (V1 to configuration 1) by 0,05 min for each successive injection until the backflushed $C_{6+}$ peak area (in fact 2,2-dimethyl butane) starts to decrease.

**A.6.4**    Continue to inject the gas mixture, now reducing the backflush time by 0,05 min for each successive injection. Note the time at which the area of the $C_{6+}$ peak first becomes constant ($t_{back,high}$).

**A.6.5**    Continue to inject the gas mixture with further incremental reductions in the backflush time until the size of the $n$-pentane peak starts to decrease, with a corresponding increase in the size of the $C_{6+}$ peak. Note the latest backflush time at which the areas of both peaks are still constant ($t_{back,low}$)

**A.6.6**    Determine the value of $t_{back}$ for the backflush of column 1 (V1 → configuration 1) using the following equation

$$t_{back} = (t_{back,low} + t_{back,high}) / 2$$