
**Natural gas — Determination
of composition and associated
uncertainty by gas chromatography —**

Part 5:

**Isothermal method for nitrogen,
carbon dioxide, C₁ to C₅ hydrocarbons
and C₆₊ hydrocarbons**

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*Gaz naturel — Détermination de la composition et de l'incertitude
associée par chromatographie en phase gazeuse —*

*Partie 5: Méthode isotherme pour l'azote, le dioxyde de carbone, les
hydrocarbures C₁ à C₅ et C₆₊*



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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 www.iso.org/directives.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received www.iso.org/patents.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 193, *Natural Gas*, Subcommittee SC 1, *Analysis of Natural Gas*.

This second edition cancels and replaces the first edition (ISO 6974-5:2000).
ISO 6974 consists of the following parts, under the general title *Natural gas — Determination of composition and associated uncertainty by gas chromatography*:

- Part 1: *General guidelines and calculation of composition*
- Part 2: *Uncertainty calculations*
- Part 3: *Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C₈ using two capillary columns and one packed column*
- 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: *Isothermal method for nitrogen, carbon dioxide, C₁ to C₅ hydrocarbons and C₆₊ hydrocarbons*
- Part 6: *Determination of helium, oxygen, nitrogen, carbon dioxide and C₁ to C₈ hydrocarbons using three capillary columns*

Introduction

This part of ISO 6974 describes a method for the analysis of natural gas that is commonly used for online process applications, but can be applied to laboratory instruments. The compositional data obtained are used for the calculation of calorific value, density and Wobbe index.

It is assumed that the natural gas does not contain any oxygen at source and that any oxygen which may be present is due to contamination during sampling.

The primary use of this chromatographic method is the calculation of calorific value (CV) according to ISO 6976. It is based on a column switching technique in which multiple columns, chosen for their separating ability for particular groups of components, are switched under automatic control.

Only one injection is necessary and the first phase of the method involves accelerated backflush of C₆+ (which is measured as a recombined “pseudo component” rather than by the summation of individual component measurements). Lighter components (nitrogen, methane, carbon dioxide and ethane) are stored on the appropriate separating column while the heavier, C₃ to C₅ hydrocarbons are eluted. The lighter components are then separated by redirecting carrier gas on to the appropriate column.

A Thermal Conductivity Detector (TCD) is used for measurement of the above components.

When the method is first set up, the repeatability of measurement is established by repetitive analysis of a cylinder of test gas, commonly a typical natural gas. For each component, a control chart showing the mean value, and the bounds representing 2 and 3 standard deviations, is drawn up. Subsequently, this test gas is analysed after each calibration of the analyser, and the results are compared with the data in the control charts. The performance of the analyser is assessed by this procedure.

Any change in the method setup can give rise to differences in component responses and hence (where applied) to calculated uncertainties. In these circumstances fitting data to an existing control chart is not a suitable procedure, and the operations that were undertaken when the method was first set up shall be repeated. <https://standards.iteh.ai/catalog/standards/sist/2b4e9154-b718-47ab-ba9d-0624d2c6dd33/iso-6974-5-2014>

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

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Natural gas — Determination of composition and associated uncertainty by gas chromatography —

Part 5:

Isothermal method for nitrogen, carbon dioxide, C₁ to C₅ hydrocarbons and C₆₊ hydrocarbons

1 Scope

This part of this International Standard describes a gas chromatographic method for the quantitative determination of the content of nitrogen, carbon dioxide and C₁ to C₅ hydrocarbons individually and a composite C₆₊ measurement, which represents all hydrocarbons of carbon number 6 and above in natural gas samples. It is applicable to the analysis of gases containing constituents within the working ranges given in [Table 1](#).

Table 1 — Component working ranges

Component		Mole fraction %	
		Min.	Max.
Nitrogen	N ₂	0,1	22
Carbon dioxide	CO ₂	0,05	15
Methane	CH ₄	34	100
Ethane	C ₂ H ₆	0,1	23
Propane	C ₃ H ₈	0,05	10
iso-Butane	i-C ₄ H ₁₀	0,01	2,0
n-Butane	n-C ₄ H ₁₀	0,01	2,0
neo-Pentane	neo-C ₅ H ₁₂	0,005	0,35
iso-Pentane	i-C ₅ H ₁₂	0,005	0,35
n-Pentane	n-C ₅ H ₁₂	0,005	0,35
Hexanes +	C ₆₊	0,005	0,35

NOTE 1 The working ranges in [Table 1](#) are those for which the method has been shown to be satisfactory, and are offered for guidance. However, there is no reason why wider ranges should not be used, provided that the successful measurement of such wider ranges has been demonstrated.

NOTE 2 Hydrocarbons above n-pentane are expressed as the “pseudo-component” C₆₊ which is measured as one composite peak and calibrated as such. The properties of C₆₊ are calculated from an extended analysis of the individual C₆ and higher hydrocarbons.

NOTE 3 Oxygen is not a normal constituent of natural gas and would not be expected to be present in gas sampled to an online instrument. If any oxygen is present as a result of air contamination, it will be measured with the nitrogen. The resulting measured (nitrogen + oxygen) value will be in error to a small extent because of the slight difference between the detector responses of oxygen and nitrogen.

NOTE 4 The helium and argon contents are assumed to be sufficiently small and unvarying that they need not be analysed for.

NOTE 5 The gas sample shall not contain any hydrocarbon condensate and/or water.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6974-1, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO 6974-2, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

3 Principle

[Figure 1](#) is a flowchart showing the steps involved in the analytical process. It is based on more detailed flowcharts in ISO 6974-1 and ISO 6974-2, simplified to represent the procedure described in this part. References are given at each step to the relevant clause in this part and, where appropriate, to the relevant clauses in ISO 6974-1 and ISO 6974-2.

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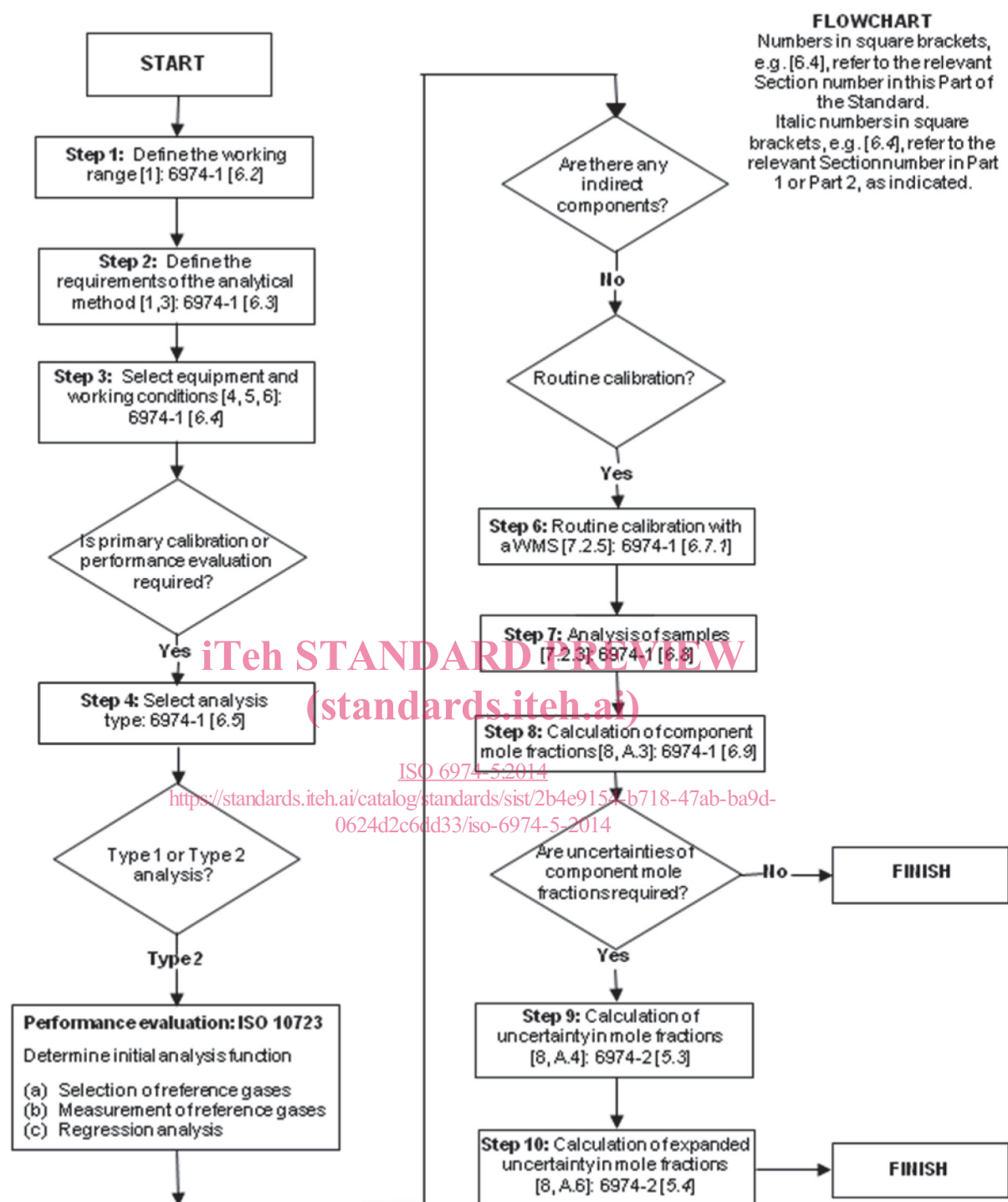


Figure 1 — Operational flowchart

NOTE The steps referred to in Figure 1 are identical to the steps in flowcharts A and B in ISO 6974-1 Step 5 refers to the use of relative response factors for indirectly measured components. Indirect components are not used in this part of ISO 6974, so step 5 is not used.

The chromatographic method uses a column switching/backflush arrangement, configured as shown in Figure 2. The sample is injected onto a boiling-point column which is divided into short and long sections (columns 1 and 2). The long section (column 2) provides separation of C₃ to C₅ hydrocarbons, while C₆ and heavier hydrocarbons are retained on the short section (column 1), from which they are

backflushed and measured by the detector as a single peak. Two six-port valves can handle the sample injection and backflushing operations, or they may be dealt with together by a single 10-port valve.

Nitrogen, carbon dioxide, methane and ethane pass rapidly and unresolved through the boiling-point column onto a porous polymer bead column (column 3), suitable for their separation. A six-port valve either connects this column or by-passes it during measurement of C₃ to C₅ components.

The separations that occur in the columns are as follows:

Column 1 Retains C₆+ 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 C₆+ has left column 1).

Column 3 Stores and separates Nitrogen, Methane, Carbon Dioxide and Ethane which elute after n-Pentane has left column 2.

4 Materials

4.1 **Carrier gas**, Helium (He), ≥99,995 % pure, free from oxygen and water.

4.2 **Auxiliary gases**, compressed air, for valve actuation (If consumption is low, carrier gas may be used as an alternative for valve actuation).

4.3 **Reference materials.**

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4.3.1 **Reference gases**, according to ISO 6974-1.

4.3.2 **Gas mixture containing n-Pentane and 2,2-Di-Me-butane**, used to check valve timings (see [Annex B](#)).

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<https://standards.iteh.ai/catalog/standards/sis/26409157-b718-47db-ba9d-0624d2c6dd33/iso-6974-5-2014>

5 Apparatus

5.1 **Gas chromatograph**, capable of isothermal operation and equipped with TCD.

5.2 **Column oven**, temperature range 70 °C to 105 °C, capable of being maintained to within ±0,1 °C.

5.3 **Valve oven**, controlled over the temperature range 70 °C to 105 °C, or valves fitted in the column oven.

5.4 **Pressure regulator**, to give suitable carrier gas flow rates

5.5 **Injection device**, V1, six-port sample injection valve

5.6 **Backflush valve**, V2, six-port, to allow rapid backflush of C₆+ components. As described in [section 3](#), a single 10-port valve may be used for both these tasks. The operating principle is the same.

5.7 **Column isolation valve**, V3, six-port. This directs the carrier gas through the porous polymer bead column (column 3), or by-passes it.

5.8 **Columns**, The columns must satisfy the performance requirements given in [7.2.4](#). The following packing materials and column dimensions, given as examples, should be satisfactory, for use with conventional and readily available injection valves and TCDs. 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.

5.9 Tube and packing.

5.9.1 Configuration 1

5.9.1.1 Column 1, 28 % DC200/500 on 45/60 mesh chromosorb P-AW, 0,75 m (2,5 foot) long, 2 mm i.d. (1/8 in o.d.).

5.9.1.2 Column 2, 28 % DC200/500 on 45/60 mesh chromosorb P-AW, 5,2 m (17 foot) long, 2 mm i.d. (1/8 in o.d.).

5.9.1.3 Column 3, 15 % DC200/500 on 50/80 mesh Porapak N, 2,4 m (8 ft) long, 2 mm i.d. (1/8 in o.d.).

5.9.2 Configuration 2.

5.9.2.1 Column 1, oxy-dipropionitrile on Porasil C, 0,3 m (1 foot) long, 0,75 mm i.d. (1/16 in o.d.).

5.9.2.2 Column 2, 20 % SF-96 on 80-100 mesh chromosorb W, 2,1 m (7 foot) long, 0,75 mm i.d. (1/16 in o.d.).

5.9.2.3 Column 3, HayeSep N, 2,1 m (7 foot) long, 0,75 mm i.d. (1/16 in o.d.).

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5.10 Method of packing, any method which results in uniform column packing may be used.

NOTE The following method is suitable. [ISO 6974-5:2014](https://standards.iteh.ai/catalog/standards/sist/2b4e9154-b718-47ab-ba9d-0624d3e61d33/iso-6974-5-2014)
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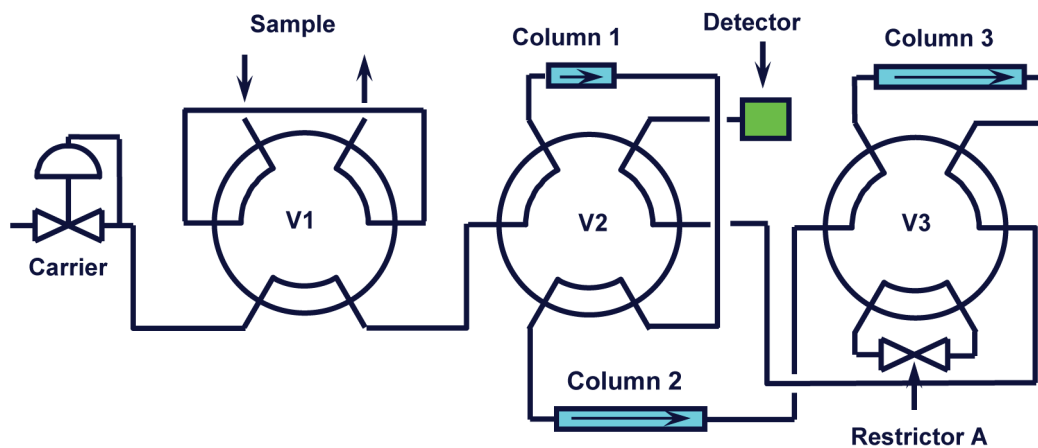
The column outlet is closed with a sintered disc or glass wool plug. A reservoir containing rather more packing than is needed to fill the column is connected to the inlet and a pressure of 0,4 MPa of nitrogen is applied to this reservoir. The flow of packing into the column is assisted by vibration. When the column is full, allow the pressure to decay slowly before disconnecting the reservoir.

5.11 Thermal Conductivity Detector (TCD), with a time constant of not greater than 0,1 s, and internal volume appropriate for the column sizes and flow rate used.

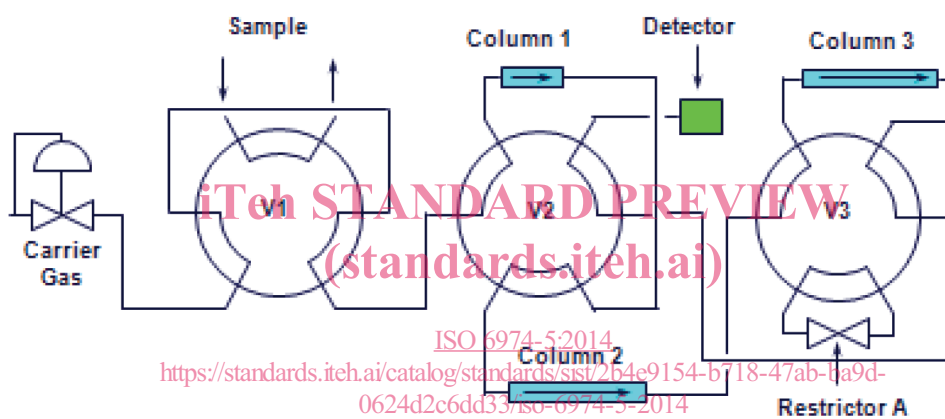
5.12 Controller/Peak Measurement System. Wide range (0 V to 1 V), capable of measuring peaks on a sloping baseline. Be enabled to control automatic operation of the valves according to a sequence selected by the operator.

5.13 Auxiliary valves, tubing and 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.

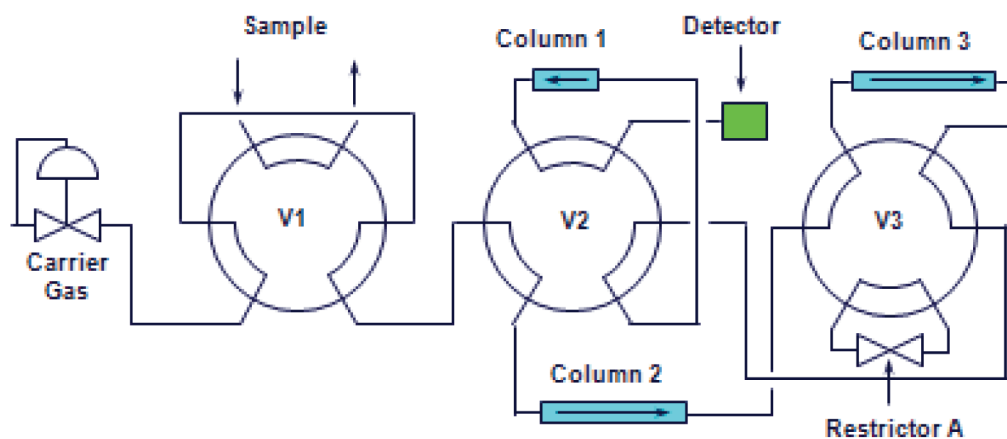
6 Scheme of the configuration



a) Initial configuration: all valves in position 1



b) Sample injection: V1 to position 2



c) Backflush C₆+: V2 to position 2