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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

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 et les hydrocarbures C1 à C5 et C6+

[Revision of first edition (ISO 6974-5:2000)]

ICS 75.060

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This draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO-lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five-month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

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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 2.

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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

This second edition cancels and replaces the first edition (ISO 6974-5:2001), [clause(s) / subclause(s) / table(s) / figure(s) / annex(es)] of which [has / have] been technically revised.

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+.*
- *Part 6: Determination of helium, oxygen, nitrogen, carbon dioxide and C1 to C10 hydrocarbons using capillary columns.*

Annexes A and B of this part of ISO 6974 are informative only

Introduction

This part of ISO 6974 describes a method for the analysis of natural gas that is commonly used for on-line 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 whilst the heavier, C₃ - 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.

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

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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+

1 Scope

Part 5 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, expressed as mole fraction % or moles/100 moles.

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

Table 1 – Component working ranges

Figure 1 is a flowchart showing the steps involved in the analytical process. It is based on more detailed flowcharts in parts 1 and 2 of this standard, 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 parts 1 and 2.

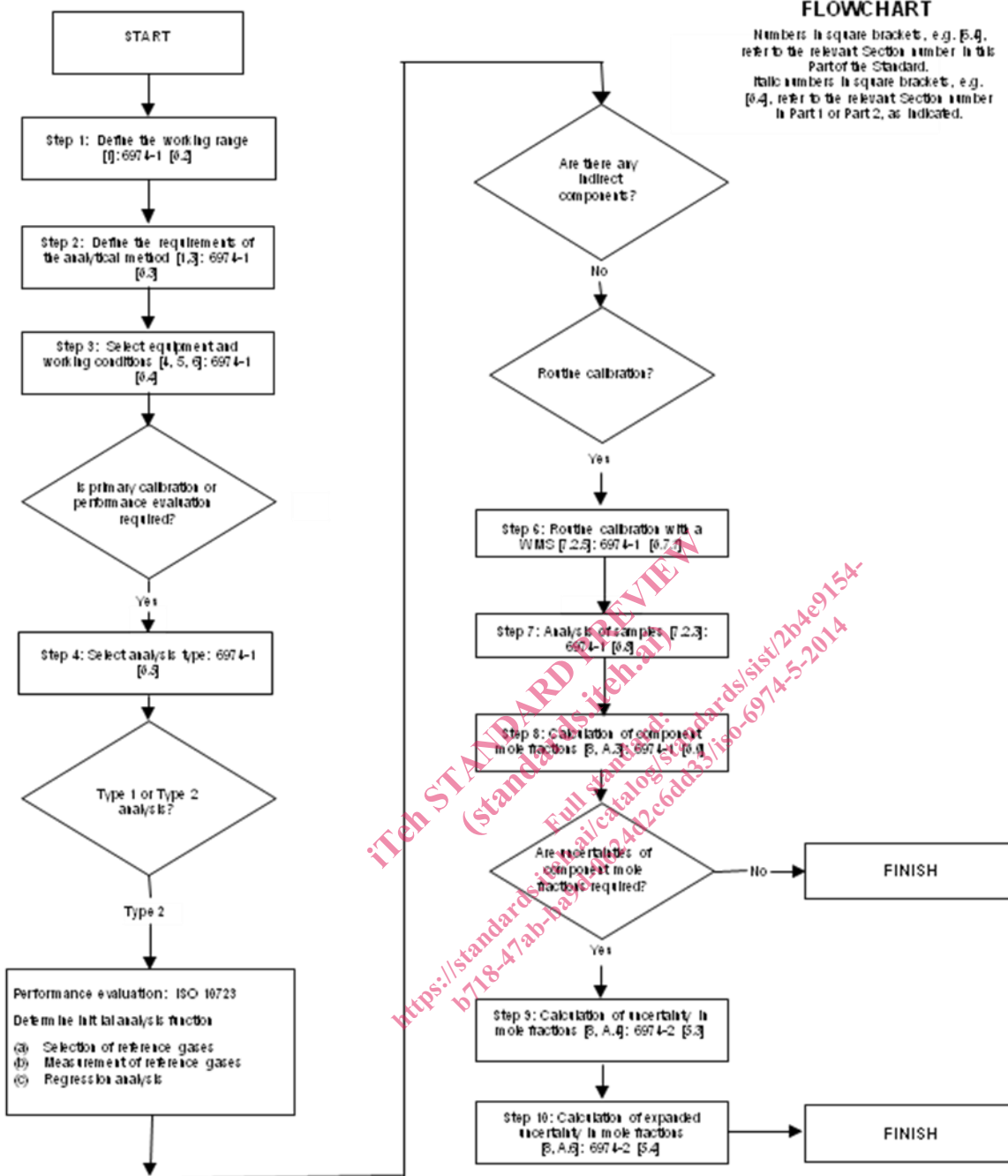


Figure 1 — Operational flowchart.

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 on-line 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 content is assumed to be sufficiently small and unvarying that helium need not be analysed for.

NOTE 5 Argon – similarly to helium.

NOTE 6 The gas sample shall not contain any hydrocarbon condensate and/or water.

2 Normative references

The following standards 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 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.*

ISO 6976, *Natural Gas – Calculation of calorific value, density, relative density and Wobbe index from compositions.*

ISO 7504, *Gas analysis – Vocabulary.*

ISO 10723, *Natural Gas – Performance evaluation for analytical systems.*

3 Principle

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 – 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 ten-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 - C₅ 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).
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), $\geq 99,995$ % 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

4.3.1 Reference gases, according to Part 1 of ISO 6974

4.3.2 n-Pentane and 2,2-Di-Me-butane, are used to check valve timings (see annex B)

5 Apparatus

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

5.2 Column oven, temperature range 70 – 105 °C, capable of being maintained to within $\pm 0,1$ °C

5.3 Valve oven, controlled over the temperature range 70 – 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 C_6+ components. As described in section 3, a single ten-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 clause 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.)

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

NOTE The following method is suitable.

The column outlet is closed with a sintered disc or glass wool plug. A reservoir containing rather more packing than is needed to fill the column is connected to the inlet and 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 to 1 volt), 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.

NOTE Auxiliary 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 Scheme of the configuration

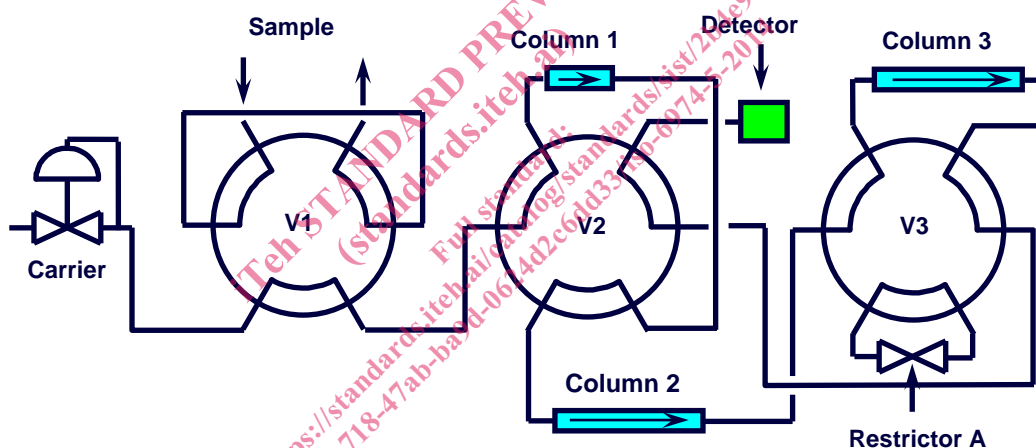


Figure 2a – Initial configuration: all valves in position 1

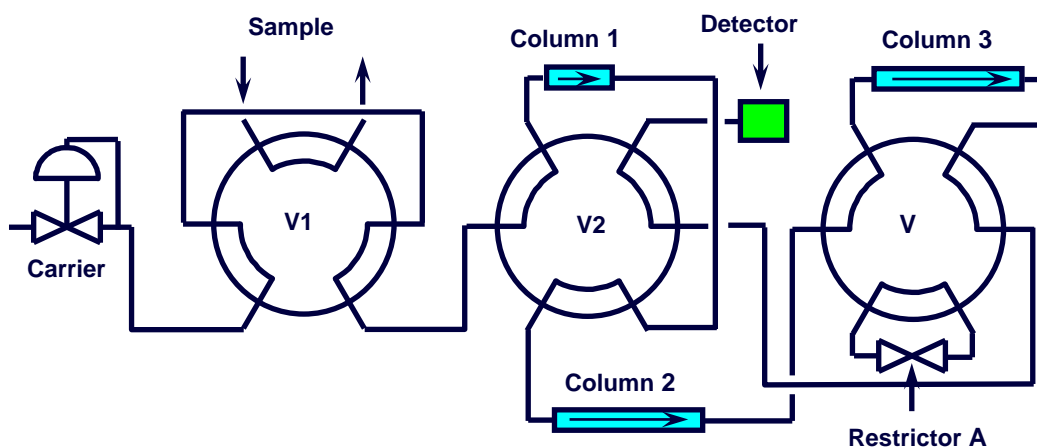


Figure 2b – Sample injection: V1 to position 2