

International Standard



6974

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Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C₈ — Gas chromatographic method

Gaz naturel — Détermination de l'hydrogène, des gaz inertes et des hydrocarbures jusqu'en C₈ — Méthode par chromatographie en phase gazeuse

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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. Every 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6974 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

Natural gas — Determination of hydrogen, inert gases and hydrocarbons up to C₈ — Gas chromatographic method

0 Introduction

This International Standard describes a precise and accurate method for the analysis of natural gas.

The method requires the use of two columns which can be put into one or two gas chromatographs. The constituents of the eluent of the first column are detected by a thermal conductivity detector (TCD). The constituents of the eluent of the second column are detected by a TCD and flame ionization detector (FID) in series.

NOTE — If the two columns are put in one chromatograph the procedure given in clause A.6 should be followed.

The detectors and associated electronics shall have a rapid response time — a time constant of not greater than 0,1 s is desired.

The method allows measurement of helium, hydrogen, oxygen, nitrogen, carbon dioxide and C₁ up to C₈ hydrocarbons.

If the content of hydrocarbons only up to C₄ or C₅ is required, reference can be made either to ISO 6568, which describes a simple method for the analysis up to C₅ of constituents of dry natural gas by gas chromatography, or to ISO 6569, which describes a rapid evaluation up to C₄ of constituents of natural gas by gas chromatography.

For analysis of natural gas for hydrocarbons from butane (C₄) up to hexadecane (C₁₆), see ISO 6975.

1 Scope and field of application

This International Standard specifies a method of quantitative analysis of the following constituents of natural gas

- helium
- hydrogen
- oxygen
- nitrogen

- carbon dioxide
- hydrocarbons from C₁ up to C₈

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

2 References

ISO 683/13, *Heat-treated steels, alloy steels and free-cutting steels — Part 13 : Wrought stainless steels.*¹⁾

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

ISO 6146, *Gas analysis — Preparation of calibration gas mixtures — Manometric method.*

ISO 6568, *Natural gas — Simple analysis by gas chromatography.*

ISO 6569, *Natural gas — Rapid analysis by gas chromatography.*

ISO 6975, *Natural gas — Determination of hydrocarbons from butane (C₄) up to hexadecane (C₁₆) — Gas chromatographic method.*²⁾

3 Principle

Separation of the components of natural gas by means of two chromatographic columns. Use of a molecular sieve 13 X³⁾ column with a TCD for the separation and detection of helium, hydrogen, oxygen and nitrogen, and a Porapak R³⁾ column with a TCD and an FID in series for the separation and detection of nitrogen, carbon dioxide and hydrocarbons from C₁ up to C₈. The two analyses are carried out independently and the results are combined.

If oxygen is seen to be present at a concentration greater than 0,02 % (mol/mol) when measuring on molecular sieve, then

1) At present at the stage of draft. (Revision of ISO 683/13-1974.)

2) At present at the stage of draft.

3) 13 X and Porapak R are trade names for commercially available products. At present, no other products intended for this purpose are known to be available commercially. This information is given for the convenience of the user of this International Standard and does not constitute an endorsement of these products by ISO.

the nitrogen value shall be taken from the molecular sieve analysis. If less than 0,02 % (mol/mol) of oxygen is present, the nitrogen value is taken from the Porapak R analysis. Quantitative results are achieved by calibration of the detectors with calibration gas mixtures. The response factors of helium, hydrogen, oxygen, nitrogen, carbon dioxide and the saturated hydrocarbons from methane up to butane are derived from an analysis of calibration gas mixtures. The relative response factors to butane of isobutane and higher hydrocarbons are given in table 5.

The resulting composition of the natural gas is normalized to 100 % (see 8.1).

4 Materials

4.1 Materials for the determination of helium, hydrogen, oxygen and nitrogen

4.1.1 Carrier gas — argon, $\geq 99,99$ % pure¹⁾, free from oxygen and water.

4.1.2 Reference materials.

4.1.2.1 Helium, oxygen and hydrogen, > 99 % pure.¹⁾

4.1.2.2 Nitrogen and methane, $> 99,99$ % pure¹⁾, free from helium, oxygen and hydrogen.

4.2 Materials for the determination of nitrogen, carbon dioxide, and hydrocarbons from C₁ up to C₈

4.2.1 Carrier gas — helium, $\geq 99,99$ % pure¹⁾, free from oxygen and water.

4.2.2 Auxiliary gases.

4.2.2.1 Hydrogen, 99,99 % pure¹⁾, free from corrosive gases, water and organic compounds.

4.2.2.2 Air, free from hydrocarbon impurities.

4.2.3 Reference materials.

4.2.3.1 Nitrogen and methane, $> 99,99$ % pure.

4.2.3.2 Carbon dioxide, ethane, propane and butane, $> 99,95$ % pure¹⁾.

Other reference materials which may be used for peak identification are pentane, hexane, heptane, octane, benzene, toluene, cyclohexane, isobutane, 2-methylbutane, neopentane and methylcyclohexane.

5 Apparatus

5.1 Apparatus for the determination of helium, hydrogen, oxygen and nitrogen

5.1.1 Gas chromatograph, capable of temperature programmed operation and equipped with a TCD.

5.1.1.1 Column oven and temperature control

5.1.1.1.1 Column oven, temperature range 35 to 350 °C, capable of being maintained to within $\pm 0,5$ °C at any temperature in the range during an analysis. To obtain a temperature of 35 °C an accessory for cooling with liquid carbon dioxide or liquid nitrogen may be necessary.

NOTE — Alternative procedures for analysis on the molecular sieve 13 X column are given in clause A.4.

5.1.1.1.2 Temperature control : The oven shall be provided with a linear programmer suitable for providing a rate of temperature increase of 30 °C/min over the specified range.

5.1.1.2 Flow regulators, to give suitable carrier gas flow rates.

NOTE — A more accurate flow controller may be used.

5.1.2 Injection device, bypass-type injector (gas sampling valve), capable of injecting a volume of 1 ml.

5.1.3 Columns

Two columns with the same type of packing and with the same dimensions (see 7.1.1.1.2).

NOTE — The second column is normally used for drift compensation during a temperature programme. If drift compensation is done by means of the electronic integrator a second column is not necessary.

5.1.3.1 Tube

- Nature : stainless steel, number 20 according to ISO 683/13 (AISI type 316), cleaned and degreased
- Length : 1 m
- Diameter : 2 mm internal diameter
- Form : appropriate to the chromatograph
- Radius : appropriate to the chromatograph

5.1.3.2 Packing

5.1.3.2.1 Molecular sieve 13 X

Particle size : 150 to 180 μm (80 to 100 ASTM mesh)

1) If the purity of the gas is less than that specified, it is essential to check that the type of impurity present does not interfere with the analysis. Also, even if the carrier gases argon and/or helium fall within the specification, some of the impurities present in these gases can nevertheless interfere with the analysis. Under these circumstances, appropriate purification is essential.

After packing, treatment overnight at approximately 350 °C with carefully dried carrier gas flowing is necessary for good separation.

5.1.3.2.2 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.

5.1.3.2.3 Efficiency of resolution

Inject a sample containing equivalent amounts (in the region of 0,4 %) of hydrogen and helium so that the height of the valley between the peaks above the baseline is not greater than 10 % of the height of the larger peak under the operation conditions stated in 7.1. If this criterion is not met continue the activation for a longer period or prepare a new column.

5.1.4 Thermal conductivity detector, with a time constant of not greater than 0,1 s.

5.1.5 Potentiometric recorder

- Range : appropriate to the detector (usually 1 to 10 mV)
- Impedance : > 2 000 Ω
- Response time : $\leq$ 0,5 s

NOTE — Alternative devices may be used provided that the requirements for response are satisfied.

5.1.6 Integrator

Wide range : 0 to 1 V

The integrator shall be capable of baseline tracking and of measuring peaks on a sloping baseline.

5.2 Apparatus for the determination of nitrogen, carbon dioxide and hydrocarbons from C₁ up to C₈

5.2.1 Gas chromatograph, for the analysis of gases suitable for dual column application equipped with a TCD and an FID in series. The FID shall have a linear dynamic range of six decades and a lower limit of detection of 10⁻¹² g/s of carbon.

5.2.1.1 Column oven and temperature control

5.2.1.1.1 Column oven, temperature range 35 to 300 °C, capable of being maintained to within $\pm$ 0,5 °C at any temperature in the range during an analysis. To obtain a

temperature of 35 °C an accessory for cooling with liquid carbon dioxide or liquid nitrogen may be necessary.

5.2.1.1.2 Temperature control : the oven shall be provided with a linear programmer suitable for providing a rate of temperature change of 15 °C/min over the specified range.

5.2.1.2 Flow regulators, to give suitable carrier gas flow rates.

NOTE — A more accurate flow controller may be used.

5.2.2 Injection device, bypass-type injector (gas sampling valve), with heating device, capable of injecting a volume of 0,5 ml.

5.2.3 Columns

Two columns with the same type of packing and with the same dimensions (see 7.2.1.1.2).

NOTE — The second column is normally used for drift compensation during a temperature programme. If drift compensation is done by means of the electronic integrator a second column is not necessary.

5.2.3.1 Tube

- Nature : stainless steel, number 20 according to ISO 683/13 (AISI type 316), cleaned and degreased
- Length : 3 m
- Diameter : 2 mm internal diameter
- Form : appropriate to the chromatograph
- Radius : appropriate to the chromatograph

5.2.3.2 Packing

5.2.3.2.1 Porapak R

Particle size : 150 to 180 μ m (80 to 100 ASTM mesh)

After packing, treatment overnight at approximately 230 °C with carefully dried carrier gas flowing is necessary for good separation.

5.2.3.2.2 Method of packing

Any method which results in uniform column packing may be used. A suitable method is described in the note to 5.1.3.2.2.

5.2.3.2.3 Efficiency of resolution

Inject a natural gas sample so that the height of the valley between the 2-methylbutane and pentane peaks above the baseline is not greater than 10 % of the height of the larger peak under the operation conditions stated in 7.2. If this criterion is not met continue the activation for a longer period or prepare a new column.