# INTERNATIONAL STANDARD

**ISO**

**6975**

Second edition
1997-04-01

# Natural gas — Extended analysis — Gas-chromatographic method

*Gaz naturel — Analyse étendue — Méthode par chromatographie en phase gazeuse*

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**Annexes**

# 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.

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.

International Standard ISO 6975 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 6975:1986), which has been technically revised.

Annexes A to D of this International Standard are for information only.

# Introduction

This International Standard describes the specifications that an accurate method for the complete and extended analysis of natural gas shall fulfil.

The analytical methods involve injection of natural gas on to packed or open tubular (capillary) columns in one or more gas chromatographs. The components coming off the columns are detected by thermal-conductivity detector (TCD) or flame ionization detector (FID).

Compared to other analytical methods, the extended gas-chromatographic analysis supplies considerable knowledge of the individual components in the natural-gas mixture. This allows quantitative measurement of particular components in the $C_{6+}$ fraction and calculation of physical properties. Although the higher hydrocarbons influence physical properties such as calorific values and density by less than 0,3 % and 0,004 %, respectively, knowledge of them is required for evaluation of the pseudo-values for the $C_{6+}$ fraction.

In addition, vapour phase equilibrium calculations often require detailed composition data, especially of hydrocarbons with carbon numbers higher than 6.

The simultaneous determination of benzene and other aromatics is needed for gas consumers using natural gas as a chemical feedstock since these components can interfere in some processes.

# Natural gas — Extended analysis — Gas-chromatographic method

## 1 Scope

This International Standard describes the specifications for the quantitative analysis of the following components of natural gas:

helium

hydrogen

argon

oxygen

nitrogen

carbon dioxide

saturated hydrocarbons from $C_1$ to $C_5$

hydrocarbon fractions from $C_6$ upwards

aromatic compounds as benzene and toluene

The gas-chromatographic methods determine the components in the following ranges:

| | | | |
|---|---|---|---|
| oxygen: | 0,001 % ($n/n$) | to | 0,5 % ($n/n$) |
| helium: | 0,001 % ($n/n$) | to | 0,5 % ($n/n$) |
| hydrogen: | 0,001 % ($n/n$) | to | 0,5 % ($n/n$) |
| argon: | 0,001 % ($n/n$) | to | 0,5 % ($n/n$) |
| nitrogen: | 0,001 % ($n/n$) | to | 40 % ($n/n$) |
| carbon dioxide: | 0,001 % ($n/n$) | to | 40 % ($n/n$) |
| methane: | 50 % ($n/n$) | to | 100 % ($n/n$) |
| ethane: | 0,02 % ($n/n$) | to | 15 % ($n/n$) |
| propane: | 0,001 % ($n/n$) | to | 5 % ($n/n$) |

higher hydrocarbons: The method can measure hydrocarbon components from $10^{-6}$ ($n/n$) up to their maximum concentration, which is compatible with the requirement that the gas is free from hydrocarbon condensate at any pressure in the range $1 \times 10^2$ kPa to $7 \times 10^3$ kPa.

This method is not intended for the determination of oxygen compounds (water vapour, methanol, glycols) or sulfur compounds.

It is not possible to make unambiguous identifications of hydrocarbons above $C_6$. Even where "spiking" a gas mixture with known components shows where they elute, it cannot be stated with certainty that such a component is the only one with that retention time. Unidentified components are classified according to the carbon number which the analysis indicates to be appropriate. While this is a necessary simplification, it does allow a reasonable quantitative value to be obtained.

This method is intended for use in situations where the hexanes plus compositional breakdown and/or the complete analysis is desired.

The method is not intended for dense phase gases whose pressure exceeds the cricondebar (critical condensation pressure), or for gas samples containing any measurable hydrocarbon condensate, liquid water or process fluid such as methanol or glycols (see ISO 6570-1 and ISO 10715).

Gases which have been treated for transmission are unlikely to contain detectable levels of hydrocarbons above $C_{12}$. Samples taken from nearer the well head, before the gas has reached gas treatment plants, may contain hydrocarbons to $C_{16}$ or above.

## 2  Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions.*

ISO 6142:1981, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

ISO 6143:1981, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

ISO 6326-1:1989, *Natural gas — Determination of sulfur compounds — Part 1: General introduction.*

ISO 6326-2:1981, *Gas analysis — Determination of sulfur compounds in natural gas — Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds.*

ISO 6326-3:1989, *Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry.*

ISO 6326-4:1994, *Natural gas — Determination of sulfur compounds — Part 4: Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants.*

ISO 6326-5:1989, *Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method.*

ISO 6570-1:1983, *Natural gas — Determination of potential hydrocarbon liquid content — Part 1: Principles and general requirements.*

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

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1)  To be published. (Revision, in parts, of ISO 6974:1984)

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

ISO 6974-3:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, inert gases and hydrocarbons up to $C_8$.*

ISO 6974-4:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and hydrocarbons ($C_1$ up to $C_5$ and $C_{6+}$) for a laboratory and on-line measuring system.*

ISO 6974-5:—[2], *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and hydrocarbons ($C_1$ up to $C_5$ and $C_{6+}$) for a laboratory and on-line process application.*

ISO 10715:1997, *Natural gas — Sampling guidelines.*

ISO 14111:1997, *Natural gas — Guidelines for traceability in analysis.*

## 3 Definitions

For the purposes of this International Standard, the following definitions apply.

**3.1 resolution:** Gas-chromatographic resolution is a characteristic of the separation of two adjacent peaks and is measured as twice the distance between the maxima of the named peaks divided by the sum of the intercepts on the baseline made by tangents drawn to the peaks at half their height (see figure 1). The resolution $R_{AB}$ may be expressed by the following equation:

$$R_{AB} = 2 \times \frac{d_R(B) - d_R(A)}{w(B) + w(A)}$$

where

$d_R(A)$ and $d_R(B)$     are the retention distances of the eluted components A and B;

$w(A)$ and $w(B)$     are the widths of the respective peaks at their base.

**3.2 main components:** The nitrogen, carbon dioxide and saturated hydrocarbons from methane to *n*-pentane present in a natural-gas sample.

**3.3 associated components:** The helium, hydrogen, argon and oxygen present in a natural-gas sample.

**3.4 trace components:** The hydrocarbons and/or groups of hydrocarbons from *n*-pentane upwards present in a natural-gas sample.

**3.5 other components:** Those components for which this method is not intended, such as oxygen compounds (water vapour, methanol, glycol) and sulfur compounds.

**3.6 response:** The response is the output signal for a component that is measured as peak area or peak height (more often as peak area).

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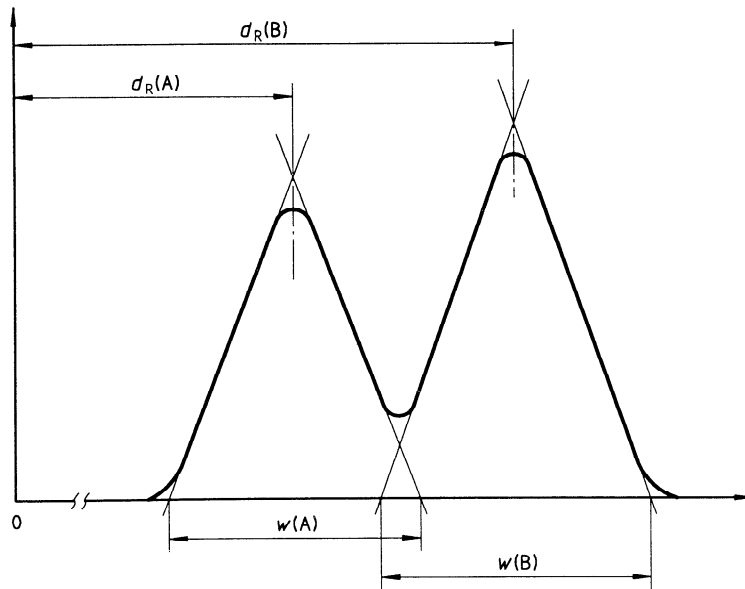2)  To be published. (Revision, in parts, of ISO 6974:1984)

**Figure 1 — Resolution of two adjacent peaks**

**3.7 reference component:** The component present in the working-reference gas mixture against which the relative response factors of sample components not present in the working-reference gas mixture are defined.

**3.8 relative response factor** (for an FID): The relative response factor $K_i$ is calculated as the ratio of the carbon number of the reference component to the carbon number of a particular sample component. Thus if the reference component is $n$-butane, then the relative response factor for $C_7$ components in the sample (heptane isomers, methylcyclohexane, toluene, etc.) is calculated as

$$K_i = \frac{4}{7} = 0,571$$

**3.9 concentration of a group of components:** The concentration of a group of components is the sum of the concentrations of the normal hydrocarbon components and their isomers. The response of the group is the sum of the responses of these components. The relative response of the group is equal to the relative response of the normal alkane of the group. The group is named according to the normal alkane of the group.

# 4 Principle

The components to be determined in a gaseous sample are physically separated by gas chromatography and compared with calibration data obtained under the same set of conditions.

The main components are separated using a packed or open tubular column in a gas chromatograph and detected by TCD. An FID may be used additionally.

The analytical system used separates oxygen from nitrogen to check air contamination in the sample.

The hydrocarbons from propane upwards are separated using an open tubular column in a gas chromatograph and detected by FID. The method assumes that the response of an FID to hydrocarbons is proportional to the carbon number. Hence, components not present in the calibration gas are quantified by means of knowledge of their carbon number.

Associated components can be determined by following special gas-chromatographic techniques (see e.g. the various parts of ISO 6974).

Identification of hydrocarbons is made by linear retention index calculation. The retention index $RI_i$ of a component $i$ is calculated as

$$RI_i = 100 \times \frac{t_i - t_x}{t_{(x+1)} - t_x} + 100\,x$$

where

$t_i$  is the retention time of component $i$;

$t_x$  is the retention time of an appropriate $n$-alkane of carbon number $x$;

$t_{(x+1)}$ is the retention time of an $n$-alkane of carbon number $(x+1)$.

This method of calculation was described by Hayes and Pitzer[3] (see annex D) and is true only for temperature-programmed analysis.

A list of retention indices is given in annex C.

The retention indices should be seen as indications rather than definite values. They are more valuable in indicating the difference $\Delta(RI)$ between compounds.

## 5 Analysis and analytical requirements

### 5.1 Apparatus and materials

#### 5.1.1 Analytical system

The analytical system shall consist of a gas-chromatographic unit and an integrator and data reduction system.

The gas-chromatographic unit may consist of one or more gas chromatographs capable of isothermal and/or temperature-programmed operation and equipped with a TCD and/or an FID and a sample transfer and introduction system.

Each gas chromatograph shall be connected to an integrator.

#### 5.1.2 Reference gas mixtures

##### 5.1.2.1 Certified-reference gas mixtures (CRMs)

Certified-reference gas mixtures are used for the determination of the response curves of the measuring system. CRMs can be binary or multicomponent mixtures and shall be prepared gravimetrically in accordance with ISO 6142 or certified and validated by comparison with primary-standard gas mixtures (PSMs) of closely related composition (see ISO 6143).

The composition of the CRM shall be traceable to the composition of the PSM whenever available (see ISO 14111).

In the hierarchy of reference materials, this type of gas mixture corresponds to the certified reference material.

##### 5.1.2.2 Working-reference gas mixtures (WRMs)

These mixtures are used as working standards for the regular calibration of the measuring system. WRMs can be binary or multicomponent mixtures and shall be prepared gravimetrically in accordance with ISO 6142 or certified and validated by comparison with CRMs of closely related composition (see ISO 6143).

The composition of the WRM shall be traceable to the composition of the PSM whenever available (see ISO 14111).

The concentration of trace components will be calculated with the aid of a reference component, so the WRM need only contain main components.

For the determination of the main components, a WRM containing nitrogen, carbon dioxide and normal hydrocarbons from methane to $n$-butane as a minimum is required. A second WRM containing helium, argon, hydrogen and oxygen is also required for the determination of the associated components. In both mixtures, methane shall be the complementary gas.

Optionally, a single gas mixture containing all the above-mentioned components can be used.

For safety reasons, regulations may require that a WRM containing oxygen be prepared with an inert complementary gas.

The concentration of each component in the WRM shall be within the tolerances given in table 1 relative to those expected in the sample gas.

**Table 1 — Tolerance between concentrations of components in the WRM and sample**

| Actual component concentration in sample<br>% ($n/n$) | Derivation of component concentration in WRM<br>(% relative to sample concentration) |
|---|---|
| up to 0,1 | ± 100 |
| 0,1 to 1 | ± 50 |
| 1 to 10 | ± 10 |
| 10 to 50 | ± 5 |
| 50 to 100 | ± 3 |

### 5.1.2.3 Control gas

A control gas is a high-pressure gas mixture of known composition containing all the components present in the working-reference gas mixture. A control gas can be either a sample gas with a composition determined in accordance with ISO 6143 or a multicomponent mixture prepared in accordance with ISO 6142.

A control gas is used for the determination of the mean ($\mu$) and standard deviation ($\sigma$) of the concentrations of the components detected.

## 5.2  Structure of the analysis

The analysis takes into account the following components:

$x_{mc}$: main and associated components determined by using response curves, single-point calibration or a reference component;

$x_{bc}$: trace components determined by using a reference component;

$x_{oc}$: other components that are measured by using other methodologies (see e.g. the various parts of ISO 6326).

The summation of the concentrations, in % ($n/n$), is defined as 100:

$$x_{mc} + x_{bc} + x_{oc} = 100$$

## 5.3 Resolution

### 5.3.1 Main components

The resolution between two adjacent peaks for each component from nitrogen to 2-methylpropane shall not be less than 2.

The resolution between two adjacent peaks for each component from 2-methylpropane to $n$-pentane shall not be less than 4.

In the event that a valve switching is performed in multicolumn analysis, the resolution between the peak of the component eluted before switching the valve and the peak of the component that would be eluted without the valve switching shall not be less than 4.

As oxygen is detected only to check air contamination of the sample gas, the resolution between the peaks of oxygen and nitrogen shall not be less than 1,5.

### 5.3.2 Trace components

The column used for trace components shall also be capable of separating some of the main components, i.e. hydrocarbons from $C_3$ to $C_5$.

To achieve satisfactory separation of light aromatics and cycloparaffins, the column shall be capable of the following resolution:

The ratio of the height of the ethane peak to the height of the valley between ethane and propane shall not be less than 1 500:1. For this measurement, the sample shall contain approximately 3 % ($n/n$) of ethane.

The resolution between 2-methylpropane and $n$-butane shall not be less than 4.

The resolution between $n$-pentane and $n$-hexane shall not be less than 15.

The resolution between $n$-octane and $n$-nonane shall not be less than 30.

NOTE — If such measurements are made from recorder charts, different conditions from those normally chosen to display the chromatogram will be necessary. Thus two analyses at very different attenuations will be needed to measure the valley between ethane and propane and the peak height of ethane.

### 5.3.3 Associated components

The resolution between two adjacent peaks shall not be less than 1,5.

## 6 Procedures

### 6.1 Setting up the analytical system

Set up all the analytical system in accordance with the manufacturer's instructions and the analytical methods chosen.

The sample cylinder and transfer line shall be heated sufficiently to avoid condensation and sorption of higher hydrocarbons in the sampling system. The sample cylinder and transfer line shall be heated to at least 10 K above the sampling temperature. Special precautions shall be taken at any spot in the system where pressure reduction occurs.

NOTE — The temperature of a natural gas will drop by approximately 0,005 K per kilopascal of pressure reduction.

## 6.2 Injection

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

Stop the purge to allow the gas to reach the temperature of the valve and ambient pressure, then inject. The working-reference gas mixture shall be injected in the same way.

NOTE — It is also possible to introduce the sample into a previously evacuated sample loop and allow it to equilibrate to ambient pressure before injection.

# 7  Calibration and control charts

## 7.1  Calibration

Main components, except $C_4$ and $C_5$ hydrocarbons, shall be analysed using multi-level calibration.

$C_4$ and $C_5$ hydrocarbons can be analysed either using single-point calibration or using relative FID response factors.

Trace components shall be analysed using relative FID response factors. The concentration of the reference component shall be less than 1 % ($n/n$).

Associated components shall be analysed using single-point calibration.

### 7.1.1  Multi-level calibration (determination of response curve)

With multi-level calibration, the response curve for the detector over the range to be analysed is determined. This is done with at least seven calibration points for each component, distributed equally over the range. These seven points shall be determined using at least seven certified-reference gas mixtures as described in 5.1.2.1.

The response curve can be determined for each component as described in annex A.

NOTES

1  Using seven calibration points for each component enables fourth-order detector behaviour to be confirmed with a high sensitivity. Third-order behaviour mostly indicates a defective detector.

2  When determining a multi-level response curve, it is preferable that the ambient pressure is constant for the whole of the calibration cycle since the amount injected is directly proportional to the ambient pressure. One way of avoiding problems is to record the ambient pressure at each injection of calibration gas and then correct the measured response to standard pressure using the following equation:

$$R_{c,st} = R_c \times \frac{p_{st}}{p_c}$$

where

   $R_{c,st}$  is the response corrected to standard pressure;

   $R_c$    is the measured response;

   $p_c$    is the ambient pressure, in kilopascals;

   $p_{st}$   is standard atmospheric pressure (101,325 kPa).

### 7.1.2  Single-point calibration (determination of response curve)

Single-point calibration is used on the assumption that the detector behaviour intercepts the origin and is linear over a small range around the point at which the chromatograph is calibrated.