INTERNATIONAL STANDARD

ISO 6974-3

First edition
2000-04-01

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

Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C8 using two packed columns

Gaz naturel — Détermination de la composition avec une incertitude définie par chromatographie en phase gazeuse — Partie 3: Détermination de l'hydrogène, de l'hélium, de l'oxygène, de l'azote, du dioxyde de carbone et des hydrocarbures jusqu'à C8 à l'aide de deux colonnes remplies

Reference number
ISO 6974-3:2000(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

Contents

Page

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 6974-3 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 analysis of natural gas, which permits the determination of the composition of natural gas. The compositional data obtained are used for the calculation of calorific value, relative density and the Wobbe index.

This method requires the use of two columns which are 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 (FID) in series.

If the two columns are put into one chromatograph the gas chromatographic conditions are described in informative annex A.

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 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C8 using two packed columns

1 Scope

This part of ISO 6974 describes a gas chromatographic method for the quantitative determination of the content of helium, hydrogen, oxygen, nitrogen, carbon dioxide and C_1 to C_8 hydrocarbons in natural gas samples using two packed columns. This method is applicable to determinations made in on-line processes or in the laboratory. It is applicable to the analysis of gases containing constituents within the mole fraction ranges given in Table 1 and which do not contain any hydrocarbon condensate. 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 in conjunction with parts 1 and 2 of ISO 6974.

Table 1 — Application ranges

Component	Mole fraction range %
Helium	0,01 to 0,5
Hydrogen	0,01 to 0,5
Oxygen	0,1 to 0,5
Nitrogen	0,1 to 40
Carbon dioxide	0,1 to 30
Methane	50 to 100
Ethane	0,1 to 15
Propane	0,001 to 5
Butanes	0,000 1 to 2
Pentanes	0,000 1 to 1
Hexanes to octanes	0,000 1 to 0,5

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 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, *Gas analysis — Vocabulary.*

3 Principle

Determination of nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8 by gas chromatography using two chromatographic columns. A molecular sieve 13X column coupled with a thermal conductivity detector (TCD) is used for the separation and detection of hydrogen, helium, oxygen and nitrogen, and a Porapak R column coupled with a TCD and a flame ionization detector (FID) in series is used for the separation and detection of nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8. The two analyses are carried out independently and the results are combined.

If oxygen is seen to be present at a mole fraction greater than 0,02 % when measured using the molecular sieve column, then the nitrogen value shall be taken from the molecular sieve analysis. If the mole fraction of oxygen is less than 0,02 % and assuming that hydrogen is absent from the gas sample, the nitrogen value can be taken from the Porapak R analysis.

Quantitative results are achieved by determining the response of the TCD detector with reference-gas mixtures and using relative response factors of the FID detector.

The resulting composition of the natural gas is normalized to 100 %.

4 Materials

4.1 For the determination of helium, hydrogen, oxygen and nitrogen, (separation on molecular sieve 13X column) consisting of the following.

4.1.1 Argon carrier gas, > 99,99 % pure, free from oxygen and water.

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 the gases can nevertheless interfere with the analysis. Under these circumstances, appropriate purification is essential.

4.1.2 Working-reference gas mixtures (WRM), consisting of:

4.1.2.1 Gas mixtures containing helium and hydrogen with nitrogen or argon as the matrix gas.

4.1.2.2 Gas mixtures containing oxygen and nitrogen with argon as the matrix gas.

NOTE 1 Take care to prevent explosion of gas mixtures.

NOTE 2 In the case of analysis using only one instrument, the WRM with oxygen and nitrogen as components and argon as the matrix gas can be replaced by oxygen with nitrogen as matrix gas. By addition of helium to the WRM this gas could also be used for the daily calibration.

1) To be published.

4.2 For the determination of nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8 (separation on Porapak column), consisting of the following.

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

4.2.2 Working-reference gas mixtures (WRM), consisting of multi-component gas mixtures containing: nitrogen, carbon dioxide and hydrocarbons from C_1 to C_3 (optional to C_4)

An example of the composition of the working-reference gas mixture is given in Table 2.

Table 2 — Example of the composition of the working-reference gas mixture

Component	Mole fraction %
Nitrogen	6
Methane	80,5
Carbon dioxide	9
Ethane	4
Propane	0,5
n-Butane	0,5 (optional)

4.2.3 FID gases, consisting of

a) **hydrogen**, > 99,99 % pure, free from corrosive gases and organic compounds;

b) **air**, free from hydrocarbon impurities.

5 Apparatus

5.1 Laboratory gas chromatographic (GC) system, consisting of two columns, a molecular sieve 13X column and a Porapak column, which are contained in two column-ovens or can be placed in the same column-oven.

The gas sample is injected on each column by means of a 6-way sample valve. Signal responses of components in the gas sample are detected using TCD and/or FID detectors.

NOTE The gas sample can be injected into the Porapak and molecular sieve column in series using a column isolation technique.

5.1.1 For the determination of helium, hydrogen, oxygen and nitrogen, equipped with the following specific components and characteristics.

5.1.1.1 Gas chromatograph, capable of temperature-programmed operation and equipped with a TCD and the following specific equipment:

a) **column oven and temperature controller,** consisting of:

— **column oven**, capable of maintaining the temperature of the column to within ± 0,5 °C over a temperature range from 35 °C to 350 °C;

NOTE 1 To obtain a temperature of 35 °C when testing at high ambient temperatures, a provision for cooling may be required, for example using an accessory for cooling with liquid carbon dioxide or liquid nitrogen.

NOTE 2 Alternative procedures for analysis on the molecular sieve 13X column are given in annex A.

— **temperature controller,** consisting of a linear programmer suitable for providing a rate of temperature increase of 30 °C/min over the specified range.

b) **flow regulator**, capable of maintaining suitable carrier-gas flow rates.

5.1.1.2 Injection device, consisting of a by-pass-type injector (gas-sampling valve) having an injection capacity of 1 ml and capable of being heated to a temperature setting of 110 °C.

The sample volume shall be reproducible such that successive runs agree within 1 % for each component.

5.1.1.3 Columns, two with the same type of packing and with the same dimensions.

The second column is normally used for drift compensation during the temperature programme. If drift is compensated by means of an electronic integrator, the second column is not necessary.

Columns shall satisfy the following requirements:

a) **metal tubing,** having the following characteristics:

— nature: stainless steel, number 20 (AISI type 316), cleaned and degreased

— length: 1 m

— diameter: 2 mm internal diameter (i.d.)

— form: appropriate for the chromatograph

— radius: appropriate for the chromatograph

NOTE If a column of 3 m is used, increase the column oven temperature to 40 °C (see annex A).

b) **packing, Molecular sieve 13X,** particle size from 150 µm to 180 µm (80 ASTM mesh to 100 ASTM mesh);

— method of packing: any suitable packing method providing uniform column packing;

— conditioning: overnight at approximately 350 °C under a flow of carefully dried carrier gas.

NOTE Some injection devices are unable to deal with temperatures above 250 °C and may cause conditioning problems.

5.1.1.4 Thermal conductivity detector (TCD).

5.1.2 For the determination of nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8, equipped with the following specific components and characteristics.

5.1.2.1 Gas chromatograph, suitable for dual-column application and equipped in series with a TCD and an FID.

a) column oven and temperature controller, consisting of:

— **column oven**, capable of maintaining the temperature of the column to within ± 0,5 °C over a temperature range from 35 °C to 230 °C.

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

— **temperature controller**, consisting of a linear programmer suitable for providing a rate of temperature increase of 15 °C/min over the specified range.

b) **flow regulator,** capable of maintaining suitable carrier-gas flow rates.

5.1.2.2 Injection device, consisting of a by-pass-type injector (gas-sampling valve) having an injection capacity of 1 ml and capable of being heated to a temperature setting of 110 °C.

5.1.2.3 Columns, two of the same type of packing and with the same dimensions.

The second column is normally used for drift compensation during the temperature programme. If drift is compensated by means of an electronic integrator, the second column is not necessary.

a) **metal tubing,** having the following characteristics:

— nature: stainless steel, number 20 (AISI type 316), cleaned and degreased

— length: 3 m

— diameter: 2 mm i.d.

— form: appropriate for the chromatograph

— radius: appropriate for the chromatograph

b) **Porapak R packing,** particle size from 150 μm to 180 μm (80 ASTM mesh to 100 ASTM mesh);

— method of packing: any suitable packing method providing uniform column packing

— conditioning: overnight at approximately 230 °C under a flow of carefully dried carrier gas

5.1.2.4 Detectors, having the following characteristics:

— for components including hydrocarbons up to C_3: thermal conductivity detector (TCD)

— for hydrocarbons from C_4 to C_8: flame ionization detector (FID)

Ethane and propane can be detected by an FID if the mole fraction is less than 1 %. In either case, the time constant shall not be greater than 0,1 s. If C_3 is used as reference component, it shall be detected by an FID.

— the TCD and FID detectors shall be connected in series

NOTE If the mole fraction of oxygen is less than 0,02 %, the nitrogen value can be taken from the Porapak R analysis, assuming that hydrogen is not present in the gas sample.

6 Procedure

6.1 Gas chromatographic operating conditions

6.1.1 For the determination of helium, hydrogen, oxygen and nitrogen

Set the operating conditions for the apparatus (5.1.1) as follows.

a) Oven and column:

— initial temperature: 35 °C for 7 min

— temperature rate: 30 °C/min to 250 °C