INTERNATIONAL STANDARD

ISO 6974-6

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

Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C_1 to C_8 hydrocarbons using three capillary columns

Gaz naturel — Détermination de la composition avec une incertitude définie par chromatographie en phase gazeuse —

Partie 6: Détermination de l'hydrogène, de l'hélium, de l'oxygène, de l'azote, du dioxyde de carbone et des hydrocarbures (C_1 à C_8) en utilisant trois colonnes capillaires

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Contents

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.

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 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.

ISO 6974-6 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This first edition of ISO 6974-6, together with ISO 6974-1, ISO 6974-2, ISO 6974-3, ISO 6974-4 and ISO 6974-5, cancels and replaces 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 processing of data*

— *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 C_1 to C_8 hydrocarbons using three capillary columns*

Annex A of this part of ISO 6974 is 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 Wobbe index.

This method requires the use of three columns which are put in two gas chromatographs.

Due to the high separation power of the capillary columns used, components, generally not present in natural gas but in some natural gas substitutes, can also be detected using this method. For the analysis of natural gas substitutes, a methanizer is used in addition.

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 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C_1 to C_8 hydrocarbons using three capillary columns

1 Scope

This part of ISO 6974 describes a gas chromatographic method for the quantitative determination of the content of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C_1 to C_8 hydrocarbons in natural gas samples using three capillary columns. It is applicable to the analysis of gases containing constituents within the mole fraction ranges given in Table 1 and is commonly used for laboratory applications. 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 present at detectable levels, the method can still be applicable.

This part of ISO 6974 is only applicable if used in conjunction with parts 1 and 2 of ISO 6974.

This method can also be applicable to the analysis of natural gas substitutes.

NOTE Additional information on the applicability of this method to the determination of natural gas substitutes is also given where relevant.

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 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6974-1:2000, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis*

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

ISO 7504, *Gas analysis — Vocabulary*

Table 1 — Application ranges

Component	Formula	Mole fraction %		
Helium	He	0,002	to	0,5
Hydrogen	H_2	0,001	to	0,5
Oxygen	O_2	0,007	to	5
Nitrogen	N_2	0,007	to	40
Methane	CH_4	40	to	100
Carbon monoxide [a]	CO	0,001	to	1
Carbon dioxide	CO_2	0,001	to	10
Ethyne (Acetylene) [a]	C_2H_2	0,001	to	0,5
Ethene [a]	C_2H_4	0,001	to	0,5
Ethane	C_2H_6	0,002	to	15
Propene [a b]	C_3H_6	0,001	to	0,5
Propane [b]	C_3H_8	0,001	to	5
i-Butane	C_4H_{10}	0,000 1	to	1
n-Butane	C_4H_{10}	0,000 1	to	1
2,2-Dimethylpropane (Neopentane)	C_5H_{12}	0,000 1	to	0,5
2-Methylbutane (*i*-Pentane)	C_5H_{12}	0,000 1	to	0,5
n-Pentane	C_5H_{12}	0,000 1	to	0,5
Cyclopentane	C_5H_{10}	0,000 1	to	0,5
2,2-Dimethylbutane	C_6H_{14}	0,000 1	to	0,5
2,3-Dimethylbutane	C_6H_{14}	0,000 1	to	0,5
2-Methylpentane	C_6H_{14}	0,000 1	to	0,5
3-Methylpentane	C_6H_{14}	0,000 1	to	0,5
n-Hexane	C_6H_{14}	0,000 1	to	0,5
Benzene	C_6H_6	0,000 1	to	0,5
Cyclohexane	C_6H_{12}	0,000 1	to	0,5
Heptanes[c]	C_7H_{16}	0,000 1	to	0,5
Methylcyclohexane	C_7H_{14}	0,000 1	to	0,5
Toluene	C_7H_8	0,000 1	to	0,5
Octanes[d]	C_8H_{18}	0,000 1	to	0,5
Xylenes[e]	C_8H_{10}	0,000 1	to	0,5

NOTE The analysis may be extended under specific conditions (e.g. greater sample volume) to hydrocarbons heavier than C_8, if present in mole fractions > 1 µmol/mol.

[a] These components are generally not present in natural gas, but in natural gas substitute.

[b] The separation of propane from propene is critical. Depending on the column in use this separation may not be achieved.

[c] Components included: *n*-heptane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2,2,3-trimethylbutane. Not all isomers can be separated from each other.

[d] Components included: *n*-octane, 2-methylheptane, 3-methylheptane, 4-methylheptane, dimethylcyclohexanes, 2,2-dimethylhexane, 2,3-dimethylhexane, 2,4-dimethylhexane, 2,5-dimethylhexane, 3,3-dimethylhexane, 3,4-dimethylhexane, 2,2,3-trimethylpentane, 2,2,4-trimethylpentane (*i*-octane), 2,3,3-trimethylpentane, 2,3,4-trimethylpentane, 2,2,3,3-tetramethylbutane. Not all isomers can be separated from each other.

[e] Components included: *o*-xylene, *m*-xylene, *p*-xylene. *m*- and *p*-xylene will not be separated from each other.

3 Principle

3.1 Analysis of natural gas samples

Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons from C_1 to C_8 by gas chromatography using three capillary columns. A PLOT[1)] precolumn is used for the separation of carbon dioxide (CO_2) and ethane (C_2H_6).

A molecular sieve PLOT column is used for the separation of the permanent gases helium (He), hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and methane (CH_4).

A thick film WCOT[2)] column coated with an apolar phase is used for the separation of the C_3 to C_8 (and heavier) hydrocarbons.

The permanent gases helium (He), hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and methane (CH_4) are detected with a thermal conductivity detector (TCD). The C_2 to C_8 hydrocarbons are detected with a flame ionization detector (FID).

3.2 Analysis of natural gas substitutes

Carbon monoxide (CO) and carbon dioxide (CO_2) are detected using an FID after reduction of the components to CH_4 by a methanizer. Use of a methanizer, makes it possible to detect CO and CO_2 at a mole fractions greater than 0,001 %. If the samples do not include CO or CO_2 or if the CO and/or the CO_2 mole fraction exceeds 0,02 %, a methanizer is not required. CO and CO_2 may then alternatively be detected with the TCD.

When analysing natural gas substitutes, the PLOT column described in 3.1 can also be used for the separation of ethyne (C_2H_2) and ethene (C_2H_4) and the molecular sieve PLOT column can also be used for the analysis of carbon monoxide (CO).

4 Materials

4.1 Carrier gases

4.1.1 **Argon** (Ar), $\geqslant$ 99,999 % pure, free from oxygen and water.

4.1.2 **Nitrogen** (N_2), $\geqslant$ 99,999 % pure or **Helium** (He) $\geqslant$ 99,999 % pure.

4.2 Auxiliary gases

4.2.1 **For FID detection:**

4.2.1.1 **Nitrogen** (N_2) or **helium** (He), $\geqslant$ 99,996 % pure.

4.2.1.2 **Air**, free from hydrocarbon impurities, i.e. the mole fraction of hydrocarbons $< 1 \times 10^{-4}$ %.

4.2.1.3 **Hydrogen** (H_2), $\geqslant$ 99,999 % pure, free from corrosive gases and organic compounds.

4.2.2 **For methanizer** (optional), when analysing natural gas substitutes:

4.2.2.1 **Hydrogen,** $\geqslant$ 99,999 % pure (may also be used as make up gas).

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1) Porous layer open tubular

2) Wall coated open tubular

4.2.2.2 **Pressurized laboratory air**, for the operation of pneumatically actuated valves.

4.3 Reference materials

4.3.1 **Working reference gas mixture** (WRM), the composition of which shall be chosen to be similar to the anticipated composition of the sample.

Mole fractions of the components shall not differ by more than the relative deviations stated in Table 2.

A cylinder of distributed natural gas, containing all the components measured by this method may also be used as the WRM. Prepare the WRM in accordance with ISO 6142 and/or certify it in accordance with ISO 6143. The WRM shall contain at least nitrogen, carbon dioxide, methane, ethane, propane, *i*-butane, *n*-butane. In the case of an indirect determination, the working reference gas mixture shall contain the reference component with a concentration in agreement with the expected concentration range. Consequently, it may be necessary to use more than one WRM.

Table 2 — Relative deviation between sample and WRM

Sample mole fraction (%)	**WRM** relative deviation (%)
0,001 to 0,1	± 100
0,1 to 1	± 50
1 to 10	± 10
10 to 50	± 5
50 to 100	± 3

4.3.2 **Performance test gases.**

4.3.2.1 **For methanizer operation** (optional), consisting of a volume fraction of 0,001 % to 0,02 % each of CH_4, CO and CO_2 in helium, for use when analysing natural gas substitutes.

4.3.2.2 **Gas containing benzene and cyclohexane**, for use in verifying peak resolution.

4.3.2.3 **Gas containing hydrogen and helium**, for use in verifying peak resolution.

5 Apparatus

5.1 **Gas chromatograph system(s),** consisting of the following components:

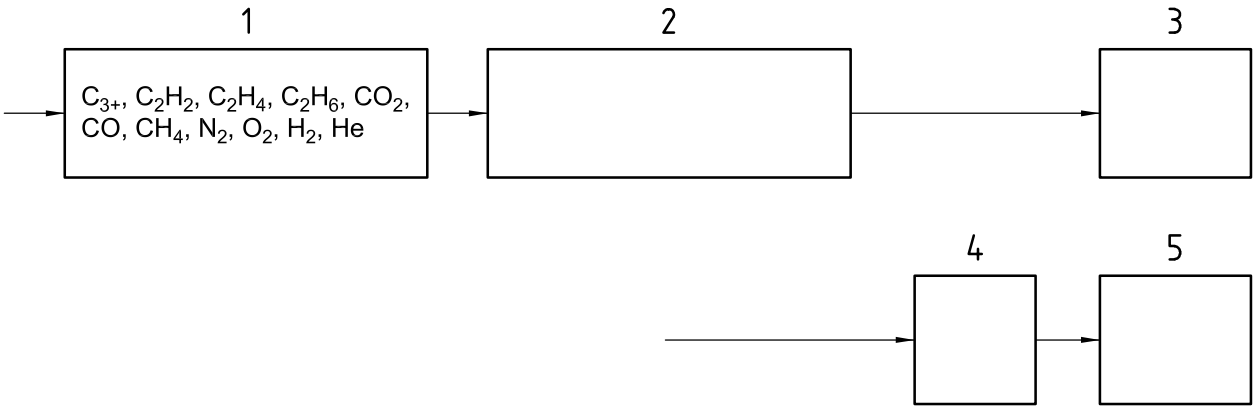
5.1.1 **Two column ovens**, for temperature-programmed operation, capable of following a given linear temperature gradient (see Table 3).

The columns may either be installed in a dual-oven gas chromatograph or in two separate instruments. The analyser should be capable of independently controlling the temperatures of both column ovens.

5.1.1.1 **Instrument 1 oven,** containing the PLOT precolumn and the molecular sieve column (see Figures 1, 2 and 3).

Instrument 1 may alternatively be equipped with a column oven for isothermal operation for a temperature range from 40 °C to 140 °C and capable of maintaining the temperature to within ± 0,1 °C at any point inside the oven chamber.

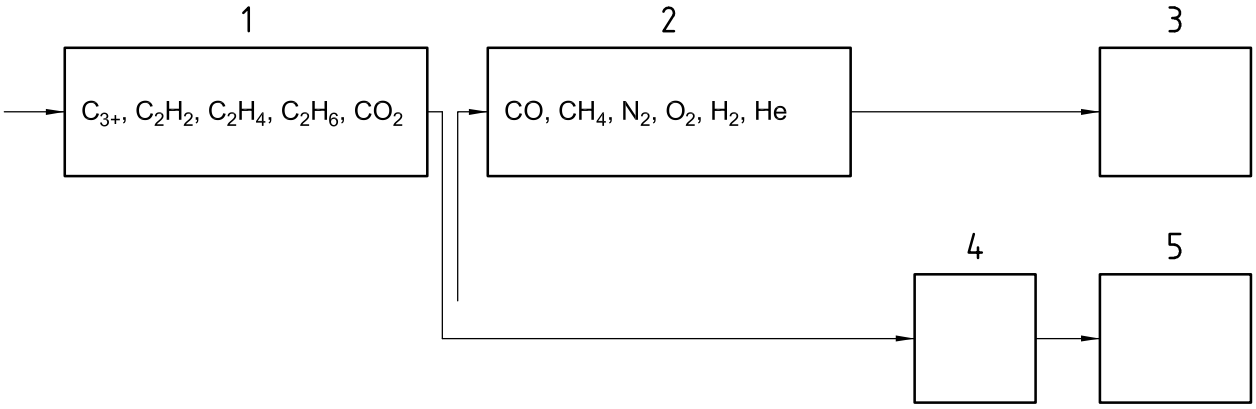
5.1.1.2 **Instrument 2 oven,** containing the WCOT column.



Key

1 Plot precolumn
2 Molecular sieve Plot column
3 TCD
4 Methanizer
5 FID

Figure 1 — Schematic diagram of the column configuration at the time of sample injection



Key

1 Plot precolumn
2 Molecular sieve PLOT column
3 TCD
4 Methanizer
5 FID

Figure 2 — Schematic diagram of the column configuration for the determination of CO_2 and C_2