भारतीय मानक

Indian Standard

IS 15130 (Part 4) : 2024
ISO 6974-4 : 2000

प्राकृतिक गैस — गैस क्रोमैटोग्राफी द्वारा संरचना और परिभाषित अनिश्चितता का निर्धारण

भाग 4 दो कॉलम का उपयोग करके एक प्रयोगशाला और ऑनलाइन माप प्रणाली के लिए नाइट्रोजन, कार्बन डाइऑक्साइड और सी$_1$ से सी$_5$ और सी$_{6+}$ हाइड्रोकार्बन का निर्धारण

(पहला पुनरीक्षण)

Natural Gas — Determination of Composition with Defined Uncertainty by Gas Chromatography

Part 4 Determination of Nitrogen, Carbon Dioxide and C_1 to C_5 and C_{6+} Hydocarbons for a Laboratory and On-line Measuring System Using Two Columns

(First Revision)

ICS 75.060

भारतीय मानक ब्यूरो

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Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (Excluding Bitumen) Sectional Committee, PCD 01

NATIONAL FOREWORD

This Indian Standard (Part 4) (First Revision) which is identical to ISO 6974-4 : 2000 'Natural gas — Determination of composition with defined uncertainty by gas chromatography — 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' issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of the Methods of Sampling and Test for Petroleum and Related Products of Natural or Synthetic Origin (Excluding Bitumen) Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

This standard was first published in 2002 and was an adoption of ISO 6974-4 : 2000 'Natural gas — Determination of composition with defined uncertainty by gas chromatography — 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. Consequent to the revision of reference standards in ISO 6974-4, the Committee decided to revise it to completely align with the latest version of reference standards.

The text of ISO standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'; and

b) Comma (,) has been used as a decimal marker while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

The other parts in this series of standard consist of the following individual parts of IS 15130.

Part 1 Guidelines for tailored analysis

Part 2 Uncertainty calculations

Part 3 Precision and bias

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

In this adopted standard, reference appears to certain International Standards for which Indian Standards also exist. The corresponding Indian Standards, which are to be substituted in their respective places, are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 6142 Gas analysis — Preparation of calibration gas mixtures — Gravimetric method	IS 16260 : 2019/ISO 6142-1 : 2015 Gas analysis — Preparation of calibration gas mixtures — Gravimetric method for class 1 mixtures (*first revision*)	Identical
ISO 6143 Gas analysis — Determination of the composition of calibration gas mixtures — Comparison methods	IS 16264 : 2014/ISO 6143 : 2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures	Identical

Contents

Page

Introduction

This part of ISO 6974 specifies a precise and accurate method for the determination of the composition of natural gas. The compositional data obtained are used for the calculation of the calorific value, the relative density and the Wobbe index. This method requires the use of two columns placed in series in a single-oven gas chromatograph.

The combination of two columns makes backflushing possible. All the constituents including the backflush peak are detected by a thermal conductivity detector (TCD).

This method is derived from ISO 6568, *Natural gas — Simple analysis by gas chromatography*.

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.

Indian Standard

NATURAL GAS — DETERMINATION OF COMPOSITION WITH DEFINED UNCERTAINTY BY GAS CHROMATOGRAPHY

PART 4 DETERMINATION OF NITROGEN, CARBON DIOXIDE AND C_1 TO C_5 AND C_{6+} HYDOCARBONS FOR A LABORATORY AND ON-LINE MEASURING SYSTEM USING TWO COLUMNS

(First Revision)

1 Scope

This part of ISO 6974 describes a gas chromatographic method for the quantitative determination of natural gas constituents using a two-column system. 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. 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 if used in conjunction with parts 1 and 2 of ISO 6974.

Table 1 — Application ranges

Component	Mole fraction range %
Nitrogen	0,001 to 15,0
Carbon dioxide	0,001 to 10
Methane	75 to 100
Ethane	0,001 to 10,0
Propane	0,001 to 3,0
iso-Butane (2-methylpropane)	0,001 to 1,0
n-Butane	0,001 to 1,0
neo-Pentane (2,2-dimethylpropane)	0,001 to 0,5
iso-Pentane (2-methylbutane)	0,001 to 0,5
n-Pentane	0,001 to 0,5
Hexanes + sum of all C_6 and higher hydrocarbons	0,001 to 0,2

NOTE 1   Oxygen is not a normal constituent of natural gas and would not be expected to be present in gas sampled for an on-line instrument. If any oxygen is present as a result of air contamination, it will be measured with the nitrogen. The resulting (nitrogen + oxygen) value will be in error to a small extent because of the slight difference between detector responses for oxygen and nitrogen. Nonetheless, the result for the natural gas/air mixture will be reasonably accurate since neither component contributes to the calorific value.

NOTE 2   The content of helium and argon are assumed to be negligible and unvarying such that helium and argon need not be determined.

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 — Determination of the composition of calibration gas mixtures — Comparison methods.*

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 7504:1984, *Gas analysis — Vocabulary.*

3   Principle

Determination of nitrogen, carbon dioxide, methane, ethane, propane, butanes and pentanes by gas chromatography using two columns (a short one and a long one) of DC-200 on Chromosorb PAW in a backflush arrangement. The short column retains hydrocarbons heavier than normal pentane which are eluted after backflushing as a C_{6+} composite peak. The long column is used for the determination of nitrogen, carbon dioxide, methane up to normal pentane. Detection is carried out by a thermal conductivity detector (TCD). Oxygen, argon, hydrogen and helium are not measured by this method.

4   Materials

4.1   Helium carrier gas, > 99,99 % pure.

4.2   Working-reference gas mixtures (WRM), the composition of which shall be chosen to be similar to that of the anticipated sample.

Prepare a cylinder of a working-reference gas mixture, by a gravimetric method, in accordance with ISO 6142, and/or certified and validated in accordance with ISO 6143. The working-reference gas mixture shall contain at least nitrogen, carbon dioxide, methane, ethane, propane, *n*-butane, *iso*-butane and possibly *neo*-pentane, *iso*-pentane and *n*-pentane.

5   Apparatus

5.1   Laboratory gas chromatographic (GC) **system,** consisting of the following components.

5.1.1   Gas chromatograph (GC), capable of isothermal operation and equipped as follows:

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1)   To be published.

a) **column oven**, capable of maintaining the temperature of the column temperature to within ± 0,1 °C over the temperature range from 70 °C to 150 °C;

b) **valve oven**: capable of being maintained over the temperature range from 70 °C to 150 °C or alternatively having the capacity to fit the valves in the column oven;

c) **flow regulators**: capable of regulating the carrier gas flow rates.

5.1.2   Injection device, consisting of a ten-port sample-injection valve V1 and also used for backflushing C_{6+} components (two six-port valves may be used for these duties).

5.1.3   Metal columns packed with 28 % DC-200 on Chromosorb PAW, satisfying the performance requirements given in clause 6.2 and consisting of the following packing materials and column dimensions, given as examples, for use with conventional and readily available injection valves and TCD.

Columns shall satisfy the following requirements:

a) metal tubing:

  ⎯ column 1: 0,45 m long, 4,75 mm internal diameter (i.d.) (1/4 in o.d.),

  ⎯ column 2: 9 m long, 4,75 mm i.d. (1/4 in o.d.)

b) packing:

  ⎯ stationary phase: 28 % DC-200 (viscosity: $350 \cdot 10^{-6}$ m^2/s),

  ⎯ support: Chromosorb PAW (45 ASTM mesh to 60 ASTM mesh),

c) method of packing: any suitable packing method providing uniform column packing and performance characteristics in accordance with 6.2. If purchased individually, as part of a system, or packed individually, their performance shall comply with the specification. When packed individually it is assumed that this will be according to a recognized technique.

  NOTE   The following packing method is suitable:

  Close the column outlet with a sintered disc or glass wool plug. Connect a reservoir containing rather more packing than is needed to fill the column to the inlet and apply a pressure of 0,4 MPa of nitrogen 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.

d) conditioning: with freshly prepared columns, more stable baselines can be obtained by conditioning them overnight, with carrier gas flowing, at a temperature of 50 °C higher than that at which they are intended to operate. If this is necessary, but not easily achieved in the gas chromatograph in which the columns are to be used, they can be conditioned after being installed in another unit.

5.1.4   Thermal conductivity detector (TCD), with a time constant no greater than 0,1 s, and internal volume appropriate for the column sizes and flow rate used.

5.1.5   Controller/peak-measurement system, having a wide range of sensitivity (0 V to 1 V), capable of measuring peaks on a sloping baseline and able to control automatic operation of the valves according to a sequence selected by the operator.

5.1.6   Auxiliary equipment, consisting of 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 Procedure

6.1 Gas chromatographic operating conditions

Set the operating conditions for the apparatus (5.1) as follows.

a) Oven column: 70 °C to 150 °C, capable of being maintained to within ± 0,1 °C.

b) Carrier gas flow rate: with the carrier gas flowing through columns in the order of column 1 toward column 2 [Figure 1 b), configuration 2], set the flow rate so as to obtain an average linear velocity for nitrogen (total column length divided by hold-up time) between 5 cm/s to 10 cm/s (corresponding to a flowrate between 30 ml/min and 60 ml/min).

c) Valves: if the valves are not fitted in the column oven, set them to a temperature in the range of 70 °C to 150 °C (no less than the column temperature), isothermal and stable to ± 2 °C.

d) Detector: TCD

— temperature setting: between 120 °C and 200 °C;

— set the bridge current according to manufacturer's instructions.

e) Controller/peak-measurement system: set up in accordance with the manufacturer's instructions.

EXAMPLE   An example of the configuration is shown in Figure 1. The measuring system comprises a ten-port sample injection/backflush valve. In configuration 1 [Figure 1 a)], the sample loop is flushed by the sample gas. When the valve is switched in configuration 2 [Figure 1 a)], injection is performed. The valve is returned to configuration 1 after all the n-pentane leaves column 1 but before the lowest C_6 isomer leaves column 1 on its way to column 2.
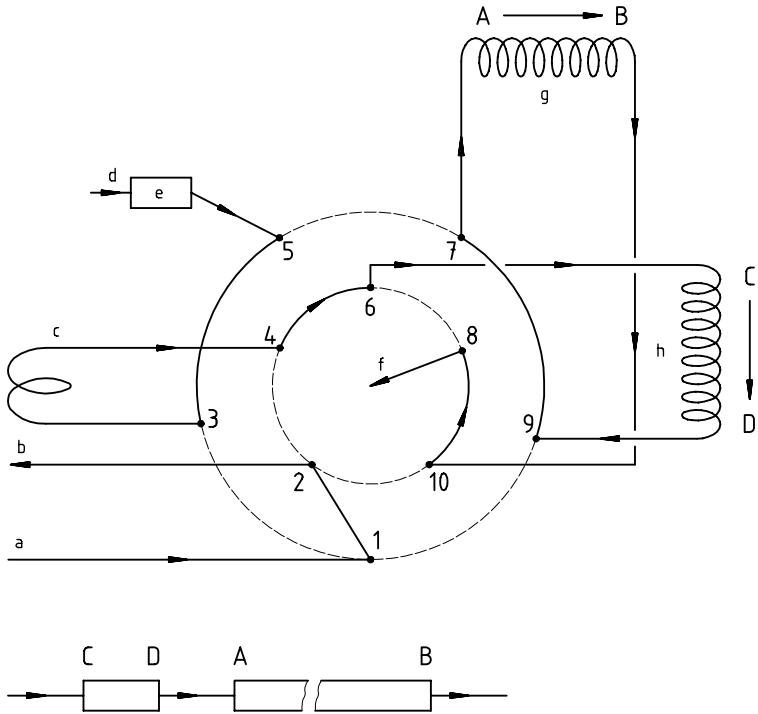
A typical chromatogram is shown in Figure 2.

The gas chromatographic conditions are summarized in Table 2.

The procedure for setting valve timings and restriction setting is described in annexes A and B.
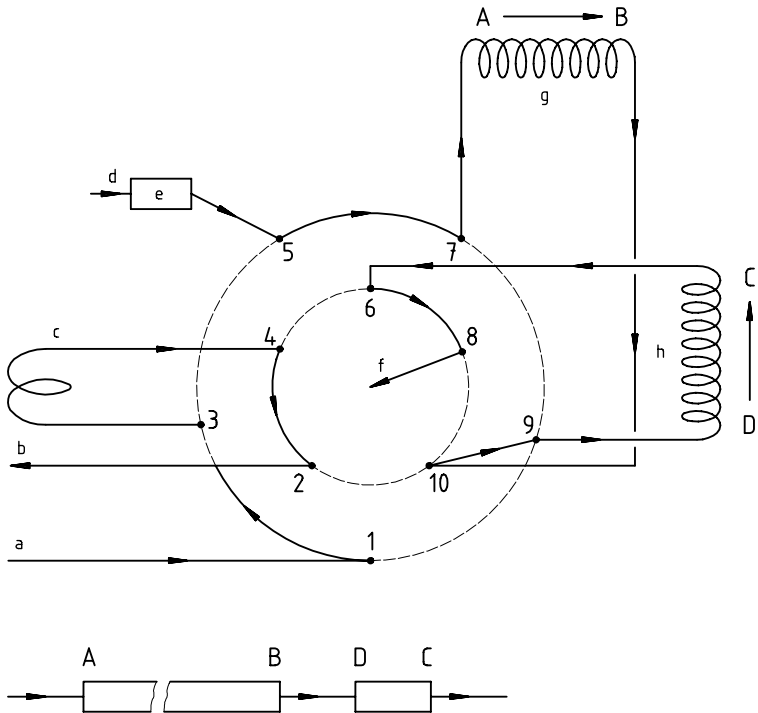
a) Configuration 1

b) Configuration 2

a	Gas sample	e	TCD (reference channel)
b	Vent	f	TCD (analysis channel)
c	Sample loop (1 ml)	g	Column 2 (length: 9 m)
d	Carrier gas	h	Column 1 (length: 0,45 m)

Figure 1 — Example of chromatograph set-up

Table 2 — Gas chromatographic conditions

| Columns	1	2
Stationary phase:	DC-200	DC-200
Loading:	28 %	28 %
Support:	Chromosorb PAW	Chromosorb PAW
Length:	0,45 m	9 m
Internal diameter, i.d.:	4,75 mm	4,75 mm
ASTM mesh size:	45 to 60	45 to 60
Column tubing:	ss or copper	ss or copper
Carrier gas		
Type:	He	
Flow:	40 ml/min	
Gas chromatograph		
Detector:	TCD	
Integrator:	External	
Injection device:	Valve	
Temperature settings		
Oven:	110 °C	
Detector:	150 °C	
Sample loop:	Oven temperature	
Transfer line	rt	
Sample	rt	
Sample volume:	1 ml	
Analysis time:	20 min.	
Abbreviations:		
ss: stainless steel		
rt: room temperature		
TCD: thermal conductivity detector		
Valve: injection and backflush device		
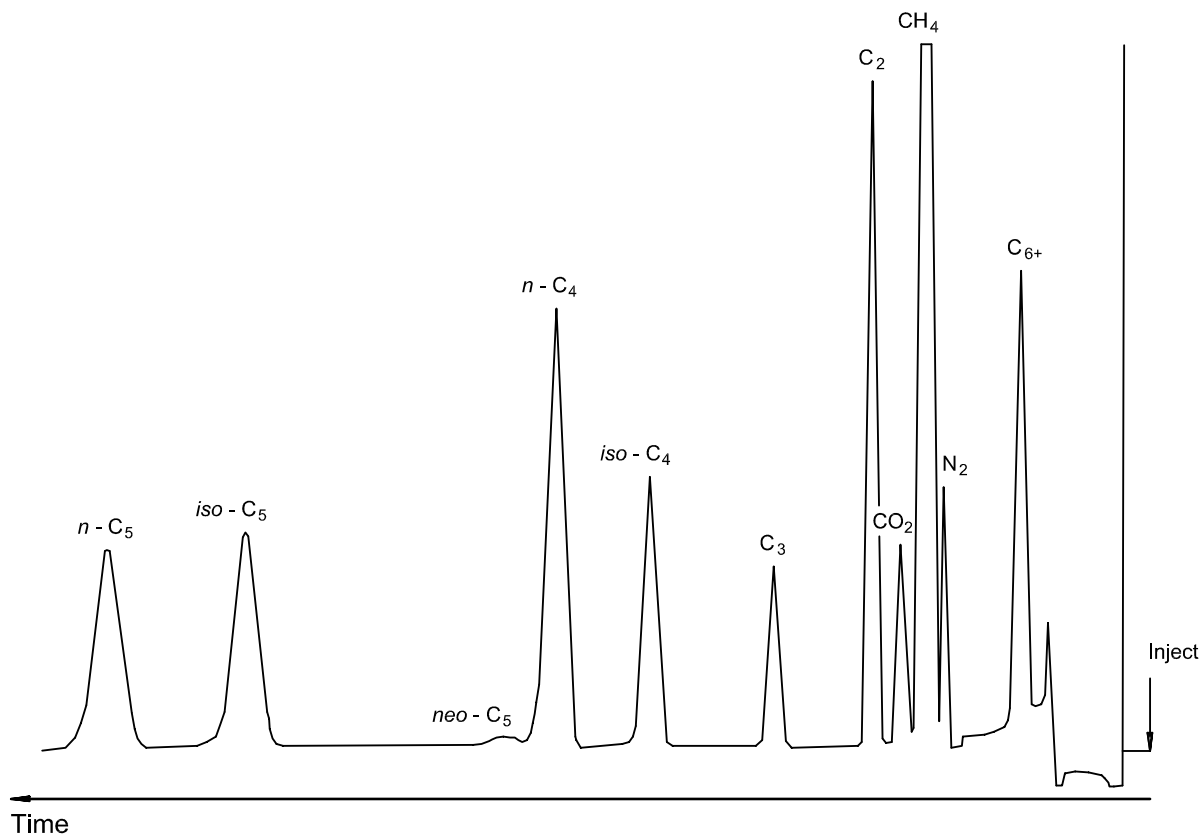
Figure 2 — Example of a typical chromatogram

6.2 Performance requirements — Peak resolution

It is important that all components are measured with as less interference from others as possible. Possible interference can be assessed by measuring peak resolution in accordance with 3.3.4.2 of ISO 7504:1984. Although the resolution of all peaks is important, there are no particular pairs of peaks which are critical. However, acceptable resolution of one pair of peaks can ensure acceptable resolution of other peaks.

Furthermore, the resolution required is likely to vary with respect to component uncertainty although it may be deemed acceptable for particular applications. If the procedure is implemented correctly, the values of acceptable peak resolution indicated in Table 3 shall be expected. Higher resolution may require modification of column dimensions, temperature and flowrate, and would likely require longer analysis time.

Each value of resolution shall be tested as part of the normal analytical cycle, not by some alternative procedure designed only to measure these parameters.

Table 3 — Acceptable peak resolution

Component 1	Component 2	Acceptable resolution
iso-Butane	*n*-Butane	2,2
Nitrogen	Methane	0,7
Carbon dioxide	Ethane	1,6

6.3 Determination — Outline of the analysis

The analysis is outlined as follows.

a) Analyse the working gas mixture and the sample in accordance with clause 11 of ISO 6974-1:2000. An example of a typical chromatogram of the analysis is given in Figure 2.

b) Measure the content of nitrogen, carbon dioxide, methane, ethane, propane, butanes and pentanes directly by means of determined response curves.

c) Oxygen, argon, hydrogen and helium are not measured by this analytical method.

d) No groups shall be determined.

e) Perform a backflush to analyse higher hydrocarbons as one composite peak (C_{6+}) and calibrate it as such.

f) Use the relative response to determine the content of pentanes when the working-reference gas mixture contains no pentanes. In this case, use *iso*-butane or *n*-butane (propane is optional) as the reference compound.

7 Expression of results

7.1 Calculation

Refer to ISO 6974-1.

7.2 Precision and accuracy

Refer to ISO 6974-2.

See annex C for typical precision values.

8 Test report

Report the results in accordance with clause 14 of ISO 6974-1:2000.

Annex A
(informative)

Procedure for setting valve timings and restriction setting

A.1 The backflush operation allows *n*-pentane (*n*-C$_5$) to be measured by forward elution and all of the lightest C$_6$ (2,2, dimethyl butane) to be backflushed. Use a gas mixture containing *n*-C$_5$ and 2,2-dimethyl butane preferably with no other C$_6$ or heavier component present.

A.2 Set the initial time to 1,5 min (or as recommended by the manufacturer) after injection at which time the valve returns to configuration 1 (see Figure 1). Inject the gas mixture and record the chromatogram. 2,2-Dimethyl butane should appear as a backflushed component (C$_{6+}$) shortly after the valve returns to configuration 1, and *n*-C$_5$ should appear as a normally eluted peak. If no C$_{6+}$ peak is seen, reduce the initial time setting and repeat this operation.

A.3 Continue to inject the gas mixture, increasing the backflush time (valve to configuration 1) by 0,05 min for each successive injection until the backflushed C$_{6+}$ peak area (in fact 2,2-dimethyl butane) starts to diminish.

A.4 Continue injecting the mixture, now reducing the backflush time setting by 0,05 min for successive injection. Note the time at which the area of the C$_{6+}$ peak first becomes constant (designated as $t_{back,high}$).

A.5 Continue injections with further incremental reductions in the backflush time until the size of the *n*-pentane peak starts to diminish, with a corresponding increase in the size of the C$_{6+}$ peak. Note the latest backflush time at which the areas of both peaks are still constant (designated as $t_{back,low}$).

A.6 Determine the value of t_{back} using the following equation

$$t_{back} = (t_{back,low} + t_{back,high}) / 2$$

Annex B
(informative)

Final time settings

Implement the method given in Table B.1 (see Figure 1).

Table B.1 — Valve configuration timing

Time	Action	Valve configuration
0,01 min	Inject	Configuration 2
t_{back}	Backflush	Configuration 1

Annex C
(informative)

Typical precision values

Typical precision values for repeatability and reproducibility are given in Table C.1.

Table C.1 — Repeatability and reproducibility of measurement results

Mole fraction x %	Repeatability		Reproducibility	
	Absolute mole fraction (%)	Relative %	Absolute mole fraction (%)	Relative %
$x < 0,1$	0,001	4,6	0,002	9,2
$0,1 < x < 1$	—	0,5	—	1
$1 < x < 50$	—	0,12	—	0,24
$50 < x < 100$	—	0,006	—	0,012
NOTE These values have been obtained from practical experience and indicate the performance of the method. They cannot be compared as such with precision values mentioned in informative annexes of other parts of ISO 6974 because they result from the quality of the calibration gases and laboratory skills employed.				

Bibliography

[1]   ISO 6976, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition.*

[2]   ISO 10723, *Natural gas — Performance evaluation for on-line analytical systems.*

International Standard	Corresponding Indian Standard	Degree of Equivalence
ISO 6974-1 : 2000 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis	IS 15130 (Part 1) : 2017/ISO 6974-1 : 2012 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis (*first revision*)	Identical
ISO 6974-2 : 2012 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for data treatment	IS 15130 (Part 2) : 2021/ISO 6974-2 : 2012 Natural Gas — Determination of composition and associated uncertainty by gas chromatography: Part 2 Uncertainty calculations (*first revision*)	Identical

The Committee has reviewed the provisions of the following International Standards referred in this adopted standard and has decided that they are acceptable for use in conjunction with this standard:

International Standard	Title
ISO 7504 : 1984	Gas analysis — Vocabulary

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

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Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the website- www.bis.gov.in or www.standardsbis.in.

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Amendments Issued Since Publication

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