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**Natural gas — Determination  
of composition and associated  
uncertainty by gas chromatography —  
Part 3:  
Precision and bias**

**iTeh STANDARD PREVIEW**  
*Gaz naturel — Détermination de la composition et de l'incertitude  
associée par chromatographie en phase gazeuse —  
Partie 3: Fidélité et biais*  
(standards.iteh.ai)

[ISO 6974-3:2018](https://standards.iteh.ai/catalog/standards/sist/8b1ad2b9-7afa-47c1-946c-eb2391058857/iso-6974-3-2018)

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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. 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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document 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 6974-3:2000), which has been technically revised.

A list of all parts in the ISO 6974 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

# Natural gas — Determination of composition and associated uncertainty by gas chromatography —

## Part 3: Precision and bias

### 1 Scope

This document describes the precision that can be expected from the gas chromatographic method that is set up in accordance with ISO 6974-1. The stated precision provides values for the magnitude of variability that can be expected between test results when the method described in ISO 6974-1 is applied in one or more competent laboratories. This document also gives guidance on the assessment of bias.

### 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

### 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at: <http://www.electropedia.org/>

#### 3.1

##### measurement precision

closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

Note 1 to entry: Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.

Note 2 to entry: The 'specified conditions' can be, for example, repeatability conditions of measurement, intermediate precision conditions of measurement, or reproducibility conditions of measurement (see ISO 5725-1).

Note 3 to entry: Measurement precision is used to define measurement repeatability, intermediate measurement precision, and measurement reproducibility.

Note 4 to entry: Sometimes "measurement precision" is erroneously used to mean measurement accuracy.

[SOURCE: JCGM 200:2012, 2.15]

### 3.2 error of measurement

measured quantity value minus a reference quantity value

Note 1 to entry: The concept of 'measurement error' can be used both

- a) when there is a single reference quantity value to refer to, which occurs if a calibration is made by means of a measurement standard with a measured quantity value having a negligible measurement uncertainty or if a conventional quantity value is given, in which case the measurement error is known, and
- b) if a measurand is supposed to be represented by a unique true quantity value of a set of true quantity values of negligible range in which case the measurement error is not known

Note 2 to entry: Measurement error should not be confused with production error or mistake.

[SOURCE: JCGM 200:2012, 2.16]

### 3.3 systematic measurement error

component of measurement error that in replicate measurements remains constant or varies in a predictable manner

Note 1 to entry: A reference quantity value for a systematic measurement error is a true quantity value, or a measured quantity value of a measurement standard of negligible measurement uncertainty, or a conventional quantity value.

Note 2 to entry: Systematic measurement error, and its causes, can be known or unknown. A correction can be applied to compensate for a known systematic measurement error.

Note 3 to entry: Systematic measurement error equals measurement error minus random measurement error.

[SOURCE: JCGM 200:2012, 2.17]

### 3.4 measurement bias

estimate of a systematic measurement error

[SOURCE: JCGM 200:2012, 2.18]

### 3.5 laboratory bias

difference between the expectation of the test results from a particular laboratory and an accepted reference value

[SOURCE: ISO 5725-1:1994, 3.9]

### 3.6 random measurement error

component of measurement error that in replicate measurements varies in an unpredictable manner

Note 1 to entry: A reference quantity value for a random measurement error is the average that would ensue from an infinite number of replicate measurements of the same measurand.

Note 2 to entry: Random measurement errors of a set of replicate measurements form a distribution that can be summarized by its expectation, which is generally assumed to be zero, and its variance.

Note 3 to entry: Random measurement error equals measurement error minus systematic measurement error.

[SOURCE: JCGM 200:2012, 2.19]

**3.7****repeatability condition of measurement**

condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

Note 1 to entry: A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

Note 2 to entry: In chemistry, the term “intra-serial precision condition of measurement” is sometimes used to designate this concept.

[SOURCE: JCGM 200:2012, 2.20]

**3.8****measurement repeatability**

measurement precision under a set of repeatability conditions of measurement

[SOURCE: JCGM 200:2012, 2.21]

**3.9****reproducibility condition of measurement**

condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

Note 1 to entry: The different measuring systems may use different measurement procedures.

Note 2 to entry: A specification should give the conditions changed and unchanged, to the extent practical.

[SOURCE: JCGM 200:2012, 2.20]

Note 3 to entry: Where repeatability is related to replicate measurements over a short period of time, reproducibility is related to replicate measurements over a longer period of time.

**3.10****measurement reproducibility**

measurement precision under reproducibility conditions of measurement

Note 1 to entry: Relevant statistical terms are given in ISO 5725-1 and ISO 5725-2.

[SOURCE: JCGM 200:2012, 2.25]

**3.11****assigned value**

value attributed to a particular property of a proficiency test item

[SOURCE: ISO 17043:2010, 3.1]

**3.12****repeatability standard deviation**

$s_r$

standard deviation of test results obtained under repeatability conditions

Note 1 to entry: It is a measure of dispersion of the distribution of test results under repeatability conditions.

Note 2 to entry: Similarly “repeatability variance” and “repeatability coefficient of variation” could be defined and used as measures of the dispersion of test results under repeatability conditions.

[SOURCE: ISO 5725-1:1994, 3.15]

### 3.13 reproducibility standard deviation

$s_R$   
standard deviation of test results obtained under reproducibility conditions

Note 1 to entry: It is a measure of dispersion of the distribution of test results under reproducibility conditions.

Note 2 to entry: Similarly “reproducibility variance” and “reproducibility coefficient of variation” could be defined and used as measures of the dispersion of test results under reproducibility conditions.

[SOURCE: ISO 5725-1:1994, 3.19]

## 4 Symbols

- $s$  standard deviation
- $s_r$  repeatability standard deviation
- $s_R$  reproducibility standard deviation
- $x_i$  amount of substance fraction of component  $i$  in the natural gas mixture

## 5 Principle

The precision data that can be expected from the gas chromatographic method that is set up in accordance with ISO 6974-1, are based on the statistical evaluation of data from 14 individual Proficiency Testing (PT) exercises that have been organized from 2012 to 2014. The precision is expressed as repeatability and reproducibility.

The scope and component ranges of these PT schemes is given in [Table 1](#).  
ISO 6974-3:2018  
<https://standards.iteh.ai/catalog/standards/sist/6b1ad269-74da-47c1-946c-eb2391058857/iso-6974-3-2018>

**Table 1 — Scope of Proficiency Testing Schemes**

	Mole fraction	
	%	
	PT Provider #1	PT Provider #2
Ethane	0,1 to 14	3 to 9
Propane	0,05 to 5	2 to 5
<i>i</i> -Butane	0,01 to 1	0,1 to 1
<i>n</i> -Butane	0,01 to 1	0,1 to 1
<i>i</i> -Pentane	0,005 to 0,35	0,02 to 0,5
<i>n</i> -Pentane	0,005 to 0,35	0,02 to 0,5
Hexane	0,001 to 0,35	0,01 to 0,1
Nitrogen	0,1 to 8	0,1 to 8
CO <sub>2</sub>	0,1 to 8	0,1 to 8
Methane	balance	65 to 99

Details on the actual data processing can be found in informative [Annex A](#).

## 6 Reference precision values

Repeatability and reproducibility standard deviations,  $s_r$  and  $s_R$  respectively, are derived from the PT data. Non-methane components are treated as a group; methane is treated separately.



For methane the repeatability standard deviation of normalized results is 0,038 % relative and the reproducibility standard deviation of normalized results is 0,09 % relative.

For all non-methane components, the repeatability standard deviation of normalized results is given by the relationship:

$$\ln(s_r) = -5,64 + 0,58 \times \ln(x_i) \quad (1)$$

And the reproducibility standard deviation of normalized results is given by the relationship:

$$\ln(s_R) = -4,28 + 0,715 \times \ln(x_i) \quad (2)$$

Typical precision values are given in [Table 2](#) and [Table 3](#).

**Table 2 — Precision of measurement results for selected methane mole fractions**

$x_i$ %	$s_r$ % Absolute	$s_R$ % Absolute
75	0,028	0,07
95	0,036	0,09

**Table 3 — Precision of measurement results for selected mole fractions for non-methane components**

$x_i$ %	$s_r$ % Absolute	$s_R$ % Absolute
0,01	0,000 25	0,000 5
0,1	0,000 938	0,002 7
1	0,003 6	0,014
10	0,014	0,072

## 7 Practical applications

The standard deviation from repeated injections under repeatability conditions can be compared to the repeatability standard deviation as given for methane or as calculated with [Formula \(1\)](#) to evaluate correct implementation of the method. It can also be used during an acceptance test for newly built equipment to evaluate performance.

The standard deviation values given in [Clause 6](#) are derived from normalised mole fraction data. Similar data shall be used for calculating precision values to be compared with those given in [Clause 6](#). The number of repeat measurements made to achieve a valid comparison is ten. If this is not possible a minimum of five measurements can be used, but the comparison will be statistically less significant. It is also important that any testing for precision follows the normal procedures used at site. So if in normal practice the data from the first injection are rejected, the laboratory should do the same for their own test data. For reproducibility it is important to check the data set for normal distribution (for example Anderson-Darling statistic[5]).

Laboratories can evaluate laboratory precision using Statistical Quality Control. Periodic injection of a Working Measurement Standard over a longer period of time, as described in ISO 6974-1 can be used to estimate the site precision. The value for this laboratory precision should be compared to the value for  $s_R$  as calculated using [Formula \(2\)](#) for non-methane components and given for methane. For this comparison a chi-squared test should be used to test if the differences between the observed laboratory precision and the reference values given in [Clause 6](#) are significant from a statistical point of view.