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

Part 1:

**General guidelines and calculation of
composition**

iTeh STANDARD PREVIEW

(standards.iteh.ai)

*Gaz naturel — Détermination de la composition et de l'incertitude
associée par chromatographie en phase gazeuse —*

Partie 1: Lignes directrices générales et calcul de la composition
ISO 6974-1:2012

<https://standards.iteh.ai/catalog/standards/sist/03f88e8b-b1c9-4e58-8618-279144a157d8/iso-6974-1-2012>



iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 6974-1:2012
<https://standards.iteh.ai/catalog/standards/sist/03f88e8b-b1c9-4e58-8618-279144a157d8/iso-6974-1-2012>



COPYRIGHT PROTECTED DOCUMENT

© ISO 2012

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Symbols	5
4.1 Symbols	5
4.2 Subscripts	6
5 Principles of analysis	6
5.1 General considerations	6
5.2 Method of operation	7
5.3 Mode of operation	8
5.4 Directly and indirectly measured components	8
5.5 Normalization	8
6 Analytical procedure	8
6.1 General considerations	8
6.2 Step 1 — Defining the working range	10
6.3 Step 2 — Defining the requirements of the analytical method	11
6.4 Step 3 — Selecting equipment and working conditions	11
6.5 Step 4 — Response characteristics (primary calibration or performance evaluation)	12
6.6 Step 5 — Relative response factors	15
6.7 Step 6 — Routine calibration/quality assurance check	16
6.8 Step 7 — Analysis of samples	17
6.9 Step 8 — Calculation of component mole fractions	18
7 Control chart	21
8 Test report	21
Annex A (informative) Comparative application ranges and characteristics of analytical methods described in ISO 6974-3 to ISO 6974-6	23
Annex B (informative) Alternative approach to bridging and normalization	25
Annex C (informative) Methane-by-difference approach	32
Annex D (normative) Relative response factors	33
Annex E (informative) Testing for outliers	35
Annex F (normative) Pressure correction during calibration and sample analysis	36
Annex G (informative) Software suitable for generalized least squares regression analysis	38
Annex H (informative) Use of control charts	40
Bibliography	41

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 2.

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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

This second edition of ISO 6974-1, together with ISO 6974-2:2012, cancels and replaces ISO 6974-1:2000 and ISO 6974-2:2001, which have been technically revised.

ISO 6974 consists of the following parts, under the general title *Natural gas — Determination of composition and associated uncertainty by gas chromatography*:

- Part 1: General guidelines and calculation of composition
- Part 2: Uncertainty calculations
- Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C₈ using two packed columns
- 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
- Part 5: Determination of nitrogen, carbon dioxide and C₁ to C₅ and C₆₊ hydrocarbons for a laboratory and on-line process application using three columns
- Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C₁ to C₈ hydrocarbons using three capillary columns

Future subsequent parts of ISO 6974 are planned.

Introduction

ISO 6974 describes methods of analysis of natural gas and methods for calculating component mole fractions and uncertainties. ISO 6974 is intended for the measurement of H₂, He, O₂, N₂, CO₂ and hydrocarbons, either as individual components or as a group, for example all hydrocarbons above C₅, defined as C₆₊. This approach is suitable for a range of end applications, including calibrating gas mixtures and providing natural gas composition and uncertainty data to be used in the calculation of calorific value and other additive physical properties of the gas. Details of these end applications are provided in ISO 6974-3 and subsequent parts of ISO 6974.

This part of ISO 6974 gives guidelines for the gas chromatographic analysis of natural gas and methods of data processing to determine compositions of component mole fractions.

ISO 6974-2 describes the steps required to calculate the uncertainty of each component mole fraction.

ISO 6974-3 and subsequent parts of ISO 6974 describe different gas chromatographic methods. These methods cover both daily practice in the laboratory and on-line field applications. In this part of ISO 6974, Annex A provides a comparison of the characteristics of the analytical methods described in ISO 6974-3 and subsequent parts of ISO 6974.

In cases where only component mole fractions are required, it is intended that this part of ISO 6974 be used in conjunction with a gas chromatographic method of analysis, e.g. ISO 6974-3 or subsequent parts of ISO 6974. In cases where component mole fractions and associated uncertainties are required, it is intended that this part of ISO 6974 be used in conjunction with ISO 6974-2, in addition to a gas chromatographic method of analysis.

This part of ISO 6974 describes all the essential steps for setting up an analysis, including outlining the structure of the analysis, defining the working ranges and establishing the analytical procedure. When the working ranges of the components have been defined, an evaluation is carried out to determine whether components are to be considered as

- main components or groups of components to be analysed using direct measurement (directly measured components),
- components or groups of components to be analysed using indirect measurement, by reference to a different reference component in the calibration gas mixture (indirectly measured components), or
- components that are not measured and whose mole fraction can be assumed to be constant (components not measured).

This part of ISO 6974 provides for the use of three types of method: single operation, multiple operation with bridging and multiple operation without bridging. The last of these methods is a special case of a single operation method.

This part of ISO 6974 describes the conventional normalization approach for calculating processed mole fractions from raw mole fractions (see 5.5). When conventional normalization is used for multiple operations without bridging methods, the uncertainties of the calculated mole fractions will be conservative. If a more accurate assessment of uncertainty is required, an alternative approach for normalization, using the generalized least squares (GLS) method, can be used; this is described in Annex B, which is intended to be used when calculating uncertainties in accordance with ISO 6974-2. Further alternative approaches are available for calculating processed mole fractions, including methane-by-difference (see Annex C) and data harmonization (see Reference [1]).

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 6974-1:2012

<https://standards.iteh.ai/catalog/standards/sist/03f88e8b-b1c9-4e58-8618-279144a157d8/iso-6974-1-2012>

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

Part 1: General guidelines and calculation of composition

1 Scope

This part of ISO 6974 gives methods for calculating component mole fractions of natural gas and specifies the data processing requirements for determining component mole fractions. This part of ISO 6974 provides for both single and multiple operation methods and either multi-point calibration or a performance evaluation of the analyser followed by single-point calibration. This part of ISO 6974 gives procedures for the calculation of the raw and processed (e.g. normalized) mole fractions, and their associated uncertainties, for all components. The procedures given in this part of ISO 6974 are applicable to the handling of data obtained from replicate or single analyses of a natural gas sample.

2 Normative references

The following referenced documents are indispensable for the application 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 Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

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

ISO 10723, *Natural gas — Performance evaluation for on-line analytical systems*

3 Terms and definitions

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

3.1

response

y

output signal of the measuring system for a component that is measured as peak area or peak height

3.2

reference component

component present in a certified reference gas mixture (CRM) (see 3.10), which is used to calibrate the analyser response to other similar components in the sample which are not themselves present in the CRM

NOTE For example, if the CRM contains hydrocarbons up to and including n -butane, but no pentanes or higher, then n -butane contained in the CRM can be used as a reference component for the quantification of pentanes and heavier components in the sample. The reference component should have a response function that normally is a first-order polynomial with zero intercept, i.e. a straight line through the origin.

3.3
relative response factor

K

ratio of the molar amount of component *j* to the molar amount of reference component which gives an equal detector response

NOTE 1 Relative response factors for flame ionization detectors are calculated as the ratio between the carbon number of the reference component and the carbon number of the sample component (see D.1).

NOTE 2 Relative response factors for thermal conductivity detectors are determined experimentally (see D.2).

3.4
other components

components in the gas sample which are not measured by analysis in accordance with ISO 6974 and/or can be regarded as being present at a constant mole fraction

3.5
group of components

components with mole fractions so low that their measurement as individuals would be difficult or require excessive time, and which are therefore measured as a group

NOTE This can be achieved by particular chromatographic techniques, such as backflushing, or by data handling, such as integrating a succession of components as if they were a single component.

3.6
uncertainty (of measurement)

parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation (or a given multiple of it), or the half-width of an interval having a stated level of confidence.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

NOTE 3 It is understood that the result of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from the systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

[ISO/IEC Guide 98-3:2008, 2.2.3]

3.7
standard uncertainty

uncertainty of the result of a measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008, 2.3.1]

3.8
combined standard uncertainty

standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[ISO/IEC Guide 98-3:2008, 2.3.4]

3.9**expanded uncertainty**

quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

NOTE 1 The fraction may be viewed as the coverage probability or level of confidence of the interval.

NOTE 2 To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

NOTE 3 Expanded uncertainty is termed *overall uncertainty* in Recommendation INC-1 (1980)^[2], Paragraph 5.

[ISO/IEC Guide 98-3:2008, 2.3.5]

3.10**certified reference gas mixture****CRM**

reference gas mixture, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

NOTE 1 The above definition is based on the definition of “certified reference material” in ISO Guide 35^[3]. “Certified reference material” is a generic term; “certified reference gas mixture” is more suited to this application.

NOTE 2 The concept of value includes qualitative attributes such as identity or sequence. Uncertainties for such attributes may be expressed as probabilities.

NOTE 3 Metrologically valid procedures for the production and certification of reference materials (such as certified reference gas mixtures) are given in, among others, ISO Guide 34^[4] and ISO Guide 35^[3].

NOTE 4 ISO Guide 31^[5] gives guidance on the contents of certificates.

3.11**working measurement standard****WMS**

measurement standard that is used routinely to calibrate or verify measuring instruments or measuring systems

[ISO/IEC Guide 99:2007^[6], 5.7]

NOTE In ISO 6974, a working measurement standard is a CRM that is used to perform a routine calibration or a quality assurance check (see 6.7).

3.12**direct measurement**

measurement by which individual components and/or groups of components are determined by comparison with identical components in the CRM(s)

3.13**indirect measurement**

measurement by which individual components and/or groups of components which are themselves not present in the CRM(s) are determined using relative response factors to a reference component in the CRM(s)

3.14**repeatability (of results of measurements)**

closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

NOTE 1 These conditions are called repeatability conditions.

NOTE 2 Repeatability conditions include:

- the same measurement procedure
- the same observer
- the same measuring instrument, used under the same conditions
- the same location
- repetition over a short period of time.

NOTE 3 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

[ISO/IEC Guide 98-3:2008, B.2.15]

3.15
working range

restricted mole fraction range specified for the methods described in ISO 6974

3.16
raw mole fraction

x^*
mole fraction of each component before the application of a process to correct the sum of the mole fractions to unity

NOTE The process of correcting the sum of mole fractions to unity is normalization or, less commonly, methane by difference.

3.17
processed mole fraction

mole fraction of each component after the application of a process to correct the sum of the mole fractions to unity

NOTE The process of correcting the sum of mole fractions to unity is normalization or, less commonly, methane by difference.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 6974-1:2012
<https://standards.iteh.ai/catalog/standards/sist/03f88e8b-b1c9-4e58-8618-279144a157d8/iso-6974-1-2012>

3.18
bridge component

component selected to allow the combination (“bridging”) of results for components measured by different analytical operations

NOTE The different operations may be two or more sample injections and/or two or more detectors.

3.19
conventional normalization

normalization whereby the sum of raw mole fractions are corrected to unity by applying the same proportional adjustment to all measured components.

NOTE A full description of conventional normalization is given in 5.5.

3.20
mean normalization

method of normalization whereby the repeat analyses for each component are averaged to form a series mean and these mean values are then normalized

NOTE Treatment of data using this method is described in 6.9.2.

3.21
run-by-run normalization

method of normalization whereby each repeat analysis is normalized independently and the average of these normalized values is then calculated

NOTE Treatment of data using this method is described in 6.9.3.

4 Symbols

4.1 Symbols

a_z	coefficients of the regression function ($z = 0, 1, 2$ or 3)
A	intermediate matrix constructed from Σ and B (see Annex B)
b_z	parameters of the regression function ($z = 0, 1, 2$ or 3)
b'_z	parameters of the regression function corrected after routine calibration (Type 1 analyses)
\bar{b}_z	mean parameters of the regression function (in “mean normalization” method)
B	matrix containing constraints (see Annex B)
D	intermediate matrix (see Annex B)
H	intermediate matrix constructed from Y , D and Σ (see Annex B)
k	coverage factor
K	relative response factor with respect to the reference component
n_{bc}	total number of bridge components
$n_{du, bc}$	total number of duplicate measurements of all bridge components ($\sum_{i=1}^{n_{bc}} [n_{du(bc_i)} - 1]$) (see Annex B)
$n_{du(...)}$	total number of duplicate measurements (of the bridge component in parentheses) (see Annex B)
n_i	total number of components (direct plus indirect, but excluding “other components”)
n_l	total number of injections (and therefore total number of responses)
p	pressure
P	parameter (see Annex H)
s	standard deviation
T	sum of raw mole fractions of all components
$u(...)$	standard uncertainty (of the quantity in parentheses)
$U(...)$	expanded uncertainty (of the quantity in parentheses)
x	normalized mole fraction (see Annex C)
x^*	raw mole fraction
x'	mole fraction calculated using the methane-by-difference approach
x^+	raw bridged mole fraction (see Annex B)
\hat{x}	adjusted mole fraction (from the calibration curve response function)
y	instrumental response of the specified analyte

\bar{y}	mean instrumental response (in “mean normalization” method)
\hat{y}	adjusted instrumental response (from the calibration curve response function)
Y	matrix accounting for the raw mole fractions of all analyses (see Annex B)
Z	matrix containing the calculated results (bridged, normalized or bridged and normalized mole fractions) (see Annex B)
$\bar{\delta}$	mean of the distribution of non-linearity errors
μ	mean (see Annex H)
Γ	measure of goodness-of-fit
Σ	variance-covariance matrix of input data (see Annex B)
ω	total number of periods (see Annex H)

4.2 Subscripts

bc	bridge component (bc ₁ , bc ₂ , ..., bc _m , where the number of bridge components = n _{bc})
br	bridging
cert	certified (given by the certificate of the CRM)
corr	corrected (by applying a correction factor)
d1, d2	detectors (where d1 and d2 are two independent detectors)
<i>i</i>	component
ind	components or groups of components to be analysed by indirect measurement
inj	(atmospheric pressure at time of) injection (see Annex F)
<i>j</i>	gas standard/mixture
<i>l</i>	injection
norm	normalization
o	original (response) at time of primary calibration or performance evaluation
oc	other components
ref	reference (component or pressure)
wms	working measurement standard
ε	period (see Annex H) (total number of periods = ω)

5 Principles of analysis

5.1 General considerations

All significant components or groups of components to be determined in a gaseous sample are physically separated by means of gas chromatography (GC) and measured by comparison with calibration data obtained under the same set of conditions. Therefore, the components within the calibration gas(es) and within the gas sample shall be analysed with the same measuring system under the same set of conditions.

The quantitative analysis of natural gas can be conducted as a single operation or through multiple operations (which may be linked by “bridge” components). Analysers can be operated in one of two modes according to the initial characterization and calibration used. There are also differences depending on whether all components are calibrated or some are measured indirectly using a “relative response” factor. As the sum of processed component mole fractions is required to equal unity, normalization is used to achieve that constraint.

The three possible methods of operation are described in 5.2.

NOTE The use of single and multiple operation methods (with or without bridging) will inevitably result in different uncertainties of the calculated mole fractions. If uncertainties are a consideration, users are advised to consider which method is most suitable for their application.

5.2 Method of operation

5.2.1 Single operation methods

In single operation methods, all measured species are determined using a single sample injection and a single detector. A special case of a single operation method is a multiple operation method without bridging, as described in 5.2.3.

5.2.2 Multiple operation methods with bridging

Multiple operation methods are based on the use of different systems (e.g. more than one injection and/or detector) to determine groups of components.

An important characteristic that distinguishes multiple operation methods with bridging from single operation methods is the fact that sample size and/or detector sensitivity may vary between groups of components. For multiple operation methods with bridging, the results of components in different groups are brought together by use of a component that is measured on each injection/detector system (a “bridge” component). The ratio of the bridge component responses is measured with every analysis, and the response values from one system are adjusted to force the ratio to be equal to that found at the time of calibration. In this way, changes in response with time are constrained to be uniform between the groups, and normalization can be applied in the same way as in the single operation method.

A component selected to act as a bridge between different parts of the analysis shall have the following characteristics:

- It is measured with good precision in each part of the analysis; the less precise of the two measurements controls how well the bridging is achieved.
- It is measured without potential interference from other components, either expected or adventitious (e.g. oxygen from air), in each part of the analysis.
- Its response in each part of the analysis over the expected working range is close to first order through the origin.

Annex B describes an alternative approach for bridging using Lagrange multipliers. This approach may be used when it is not possible to comply with the above requirements for bridging and if the user can demonstrate that compliance with Annex B gives acceptable results.

5.2.3 Multiple operation methods without bridging

Multiple operation methods without bridging are based on the use of different systems (e.g. more than one injection and/or detector) to determine groups of components, but where suitable bridge components are not available. Throughout the remainder of this part of ISO 6974, the data from these methods is treated in the same manner as data for single operation methods, of which multiple operation methods without bridging are a special case.

Systems that routinely operate as multiple operation methods without bridging include rapid, miniaturized (“micro”) gas chromatography systems.