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

**Part 2:
Uncertainty calculations**

*Gaz naturel — Détermination de la composition et de l'incertitude
associée par chromatographie en phase gazeuse — Partie 2: Calculs
d'incertitude*
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ISO 6974-2:2012

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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.

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 6974-2 was prepared by Technical Committee ISO/TC 193, *Natural Gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition of ISO 6974-2, together with ISO 6974-1:2012, 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 (all parts) 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.

ISO 6974-1 gives guidelines for calculating the mole composition of natural gas, determined using one of the gas chromatographic methods described in ISO 6974-3 and subsequent parts of ISO 6974. ISO 6974-1 also 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.

This part of ISO 6974 describes the steps required to calculate the uncertainty of the component mole fractions of natural gas determined using gas chromatography.

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. ISO 6974-1:2012, Annex A, provides a comparison of the characteristics of the analytical methods described in ISO 6974-3 and subsequent parts of ISO 6974.

It is intended that this part of ISO 6974 be used in conjunction with ISO 6974-1 and a method of analysis, e.g. ISO 6974-3 or subsequent parts of ISO 6974.

ISO 6974-1:2012, 5.5, describes the conventional normalization approach for calculating processed mole fractions from raw mole fractions. When conventional normalization is used for multiple operation methods without bridging, the uncertainties of the calculated mole fractions will be conservative. If a more accurate assessment of uncertainty is required, an alternative approach to normalization, using the generalized least squares (GLS) method, can be used; this is described in ISO 6974-1:2012, Annex B. Further alternative approaches are available for calculating processed mole fractions, including methane-by-difference (see ISO 6974-1:2012, Annex C) and data harmonization (see Reference [1]).

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

Part 2: Uncertainty calculations

1 Scope

This part of ISO 6974 describes the process required to determine the uncertainty associated with the mole fraction for each component from a natural gas analysis in accordance with ISO 6974-1.

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 6974-1:2012, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

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3 Terms and definitions

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For the purposes of this document, the terms and definitions given in ISO 6974-1 apply.

4 Symbols

4.1 Symbols

b_z	parameters of the regression function ($z = 0, 1, 2$ or 3)
\bar{b}_z	mean parameters of the regression function (in “mean normalization” method)
C_i	sensitivity coefficient
k	coverage factor
K	relative response factor with respect to the reference component
n_i	total number of components (direct plus indirect, but excluding “other components”)
n_j	total number of gas standards or mixtures
n_l	total number of injections (and therefore total number of responses)
s	standard deviation
T	total mole fraction of all raw components

$u(\dots)$	standard uncertainty (of the quantity in parentheses)
$U(\dots)$	expanded uncertainty (of the quantity in parentheses)
x	normalized mole fraction
x^*	raw mole fraction
x'	mole fraction calculated using the methane-by-difference approach [Annex A]
\hat{x}	adjusted mole fraction [Annex C]
y	instrumental response of the specified analyte
\bar{y}	mean instrumental response (in “mean normalization” method)
\hat{y}	adjusted instrumental response [Annex C]
Y	instrumental response [Annex C]
α	intercept of a first-order calibration function [Annex C]
β	gradient of a first-order calibration function [Annex C]
γ	gradient of the calibration curve [Annex C]
$\bar{\delta}$	mean of the distribution of non-linearity errors

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4.2 Subscripts

cal	calibration [Annex A]	ISO 6974-2:2012
i	component	https://standards.iteh.ai/catalog/standards/sist/6f94966a-0c3e-4e81-b7cb-31422260e749/iso-6974-2-2012
ind	components or groups of components to be analysed by indirect measurement	
j	gas standard/mixture	
l	injection	
oc	other components	
p, q	indices defining a regression coefficient	
ref	reference (component or pressure)	
s	index defining a component	
wms	working measurement standard	

5 Calculation of uncertainty

5.1 General considerations

The process of setting up a gas chromatograph for the analysis of natural gas consists of the steps outlined in the flowcharts in Figures 1 and 2.

Steps 1 to 8 are covered in ISO 6974-1. This part of ISO 6974 covers steps 9 and 10.

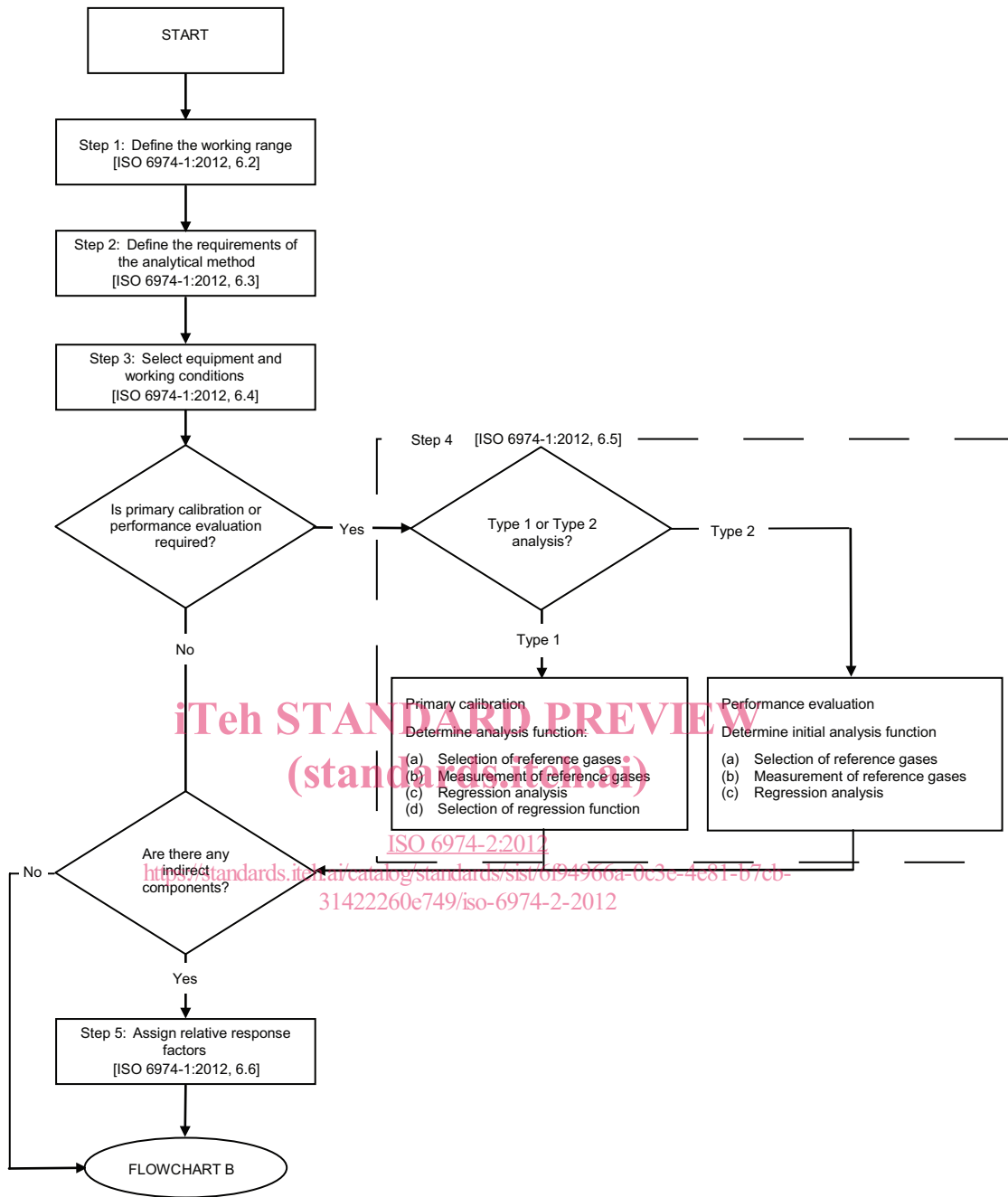


Figure 1 — Procedure for determining mole fraction and uncertainty — Steps 1 to 5

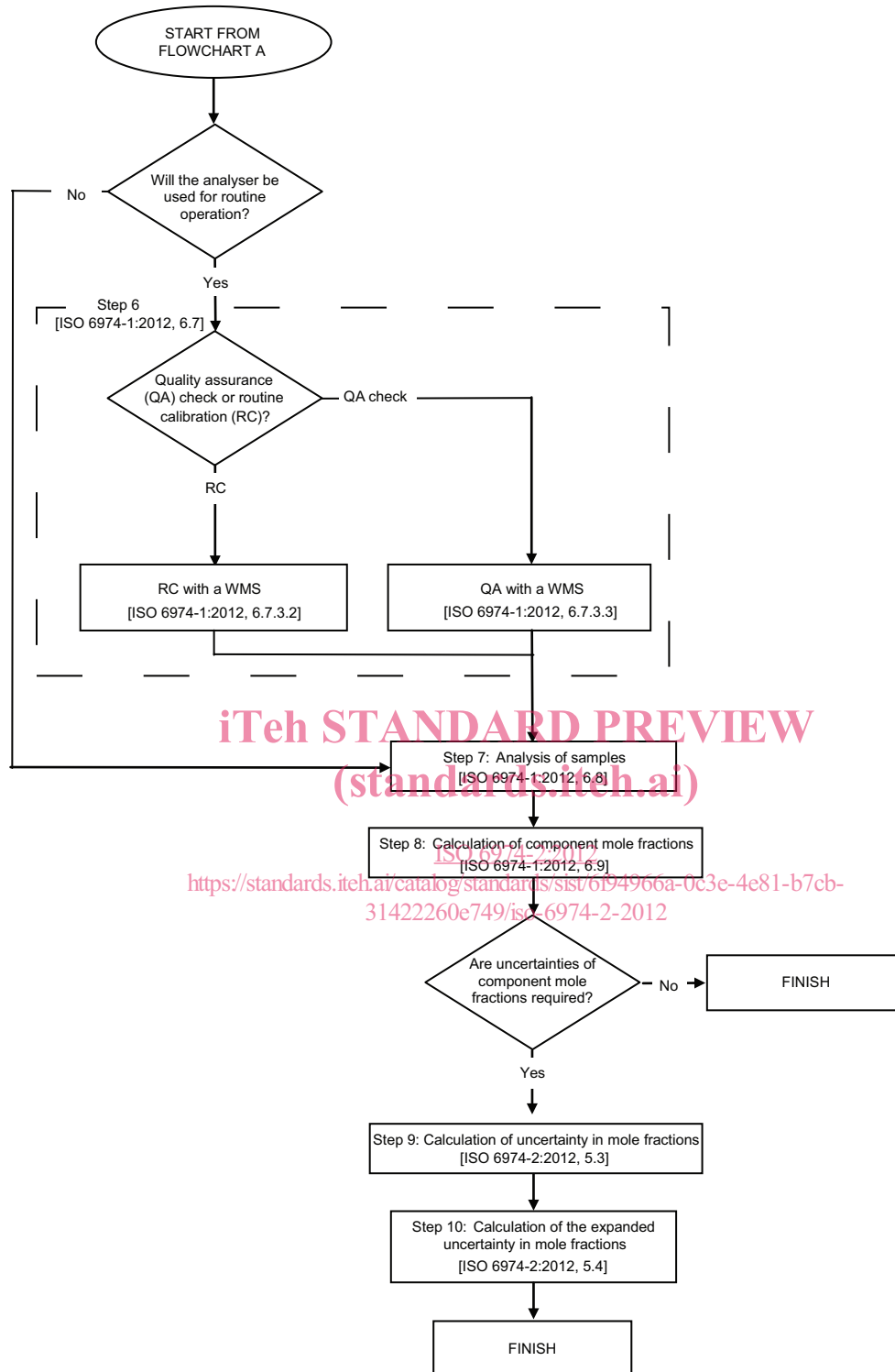


Figure 2 — Procedure for determining mole fraction and uncertainty — Steps 6 to 10

5.2 Principles

Uncertainties associated with the component mole fractions shall be calculated in accordance with ISO/IEC Guide 98-3.

For Type 1 analyses in accordance with ISO 6974-1, the uncertainty calculation includes random and systematic uncertainties from three main sources: uncertainty of the certified reference mixtures, uncertainty of analysis and uncertainty of the data fitting procedure.

For Type 2 analyses in accordance with ISO 6974-1, the uncertainty calculation includes both random elements and systematic errors introduced by the assumption of a linear response through the origin, the systematic errors being calculated from the results of the initial performance evaluation.

Subclause 5.3 describes methods for estimating the uncertainties of processed mole fractions calculated from raw mole fractions using the conventional normalization method. Annex A provides a method for use when the methane-by-difference approach (see ISO 6974-1:2012, Annex C) is employed.

ISO 6974-1 recommends the use of the generalized least squares (GLS) approach for calculation of the processed mole fraction. However, in some circumstances, an alternative approach using ordinary least squares may be acceptable and calculation of uncertainty in processed mole fractions in this situation is described in Annex C.

5.3 Step 9 — Calculation of uncertainty of mole fractions

5.3.1 Determining the equations to be used

5.3.1.1 General considerations

The equations to be used in this step for calculating the uncertainty of mole fractions are given in 5.3.2 and 5.3.3. The equations to be used should be determined by following the three-stage process described in 5.3.1.2 to 5.3.1.4.

The following points should be taken into consideration when selecting the equations to be used.

- a) When using the “mean normalization” method (see 5.3.2), the following are calculated in turn for each analyte:
 - 1) mean peak analyser response from all runs;
 - 2) raw mole fraction;
 - 3) normalized mole fraction.
- b) When using the “run-by-run normalization” method (see 5.3.3), the following are calculated in turn for each analyte:
 - 1) raw mole fraction for each run;
 - 2) normalized mole fraction for each run;
 - 3) mean normalized mole fraction.