भारतीय मानक
Indian Standard

IS 15130 (Part 1) : 2017
ISO 6974-1 : 2012

प्राकृतिक गैस — गैस वर्णलेखी पद्धति द्वारा निर्धारित संयोजन की अनिश्चितता ज्ञात करना

भाग 1 अनुकूलित विश्लेषण के लिए मार्गदर्शी सिद्धान्त

(पहला पुनरीक्षण)

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

Part 1 Guidelines for Tailored Analysis

(First Revision)

ICS 75.060

भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली–110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002
www.bis.gov.in www.standardsbis.in

June 2017 **Price Group 13**

Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee, PCD 01

NATIONAL FOREWORD

The Indian Standard (Part 1) (First Revision) which is identical with ISO 6974-1 : 2012 ‘Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis, issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of the Methods of Test for Petroleum, Petroleum Products and Lubricants Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

This standard was first published in 2002 which was an adoption of ISO 6074-1 : 2000 ‘Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis’. Consequent to revision of ISO 6974-1 in 2006, the Committee decided to revise it to completely align it with latest version of ISO Standard.

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’.

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.

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 places, are given below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 6974-2 : 2000 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) : 2002 Natural gas — Determination of composition with defined uncertainty by gas chromatography: Part 2 Measuring-system characteristics and statistics for data treatment	Identical
ISO 6974-3 : 2000 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8, using two packed columns	IS 15130 (Part 3) : 2002 Natural gas — Determination of composition with defined uncertainty by gas chromatography: Part 3 Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to C_8, using two packed columns	do
ISO 6974-4 : 2000 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 4: Determination of nitrogen, carbon dioxide and C_l to C_5 and C_{6+} hydrocarbons for a laboratory and on-line measuring system using two columns	IS 15130 (Part 4) : 2002 Natural gas — Determination of composition with defined uncertainty by gas chromatography: Part 4 Determination of nitrogen, carbon dioxide and C_l to C_5, and C_{6+} and hydrocarbons for a laboratory and on-line measuring system using two columns	do

(*Continued on third cover*)

IS 15130 (Part 1) : 2017
ISO 6974-1 : 2012

Indian Standard

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

PART 1 GUIDELINES FOR TAILORED ANALYSIS

(First Revision)

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.

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)
$\boldsymbol{A}$	intermediate matrix constructed from $\boldsymbol{\Sigma}$ and $\boldsymbol{B}$ (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)
$\boldsymbol{B}$	matrix containing constraints (see Annex B)
$\boldsymbol{D}$	intermediate matrix (see Annex B)
$\boldsymbol{H}$	intermediate matrix constructed from $\boldsymbol{Y}$, $\boldsymbol{D}$ and $\boldsymbol{\Sigma}$ (see Annex B)
k	coverage factor
K	relative response factor with respect to the reference component
n_{bc}	total number of bridge components
$n_{\mathrm{du,bc}}$	total number of duplicate measurements of all bridge components ($\sum_{i=1}^{n_{\mathrm{bc}}}\left[n_{\mathrm{du(bc}_i)}-1\right]$) (see Annex B)
$n_{\mathrm{du(...)}}$	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)
$\boldsymbol{Y}$	matrix accounting for the raw mole fractions of all analyses (see Annex B)
$\boldsymbol{Z}$	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
$\boldsymbol{\Sigma}$	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	component
ind	components or groups of components to be analysed by indirect measurement
inj	(atmospheric pressure at time of) injection (see Annex F)
j	gas standard/mixture
l	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.

The use of conventional normalization in a multiple operation method without bridging is likely to result in conservative uncertainties of the calculated mole fractions. The user should therefore consider carefully whether the use of a multiple operation method without bridging will provide an analysis that is fit for purpose.

5.3 Mode of operation

Depending on the nature of the initial characterization and calibration of an analyser, two different modes of operation can be distinguished.

A Type 1 analysis first determines response functions by means of a multi-point calibration using CRMs, followed by regression analysis. These response functions are then used to calculate component mole fractions in samples analysed against this calibration. Type 1 analyses do not involve non-linearity errors (see 6.9.4).

A Type 2 analysis assumes a response function, and subsequent sample analysis is carried out against routine calibrations using a single WMS. Because the assumed response function can differ from the true one, Type 2 analyses can have non-linearity errors, which shall be evaluated by means of a multi-point performance evaluation carried out in accordance with ISO 10723 (see 6.9.4).

5.4 Directly and indirectly measured components

A directly measured component is one that is measured and is present as a certified component in the CRM such that it is quantified directly from the calibration data for that component.

An indirectly measured component is one that is measured but is not present as a certified component in the CRM and is quantified indirectly using a relative response factor. The mole fraction of these components is determined by comparing the peak area of the indirectly measured component to that of a certified component and by applying an appropriate relative response factor (see Annex D). The use of a relative response factor (which has an inherent uncertainty) increases the uncertainty of the measured mole fraction.

5.5 Normalization

Normalization is an approach to processing the raw mole fractions that corrects the sum to unity by applying the same proportional adjustment to all measured components. It is best suited to measurements of natural gas where the dominant uncertainties are highly correlated for all components, because they are the result of effects that influence all components (such as variations in ambient air pressure and detector drift).

For a mixture with n_i components, excluding “other components”, the normalized mole fraction of component i is calculated using Equation (1):

$$x_i = \frac{x_i^*}{\sum_{i=1}^{n_i} x_i^*} \times \left(1 - x_{\text{oc}}\right) \tag{1}$$

NOTE In Annex B there is a description of an alternative approach to bridging and normalization.

6 Analytical procedure

6.1 General considerations

The process of setting up a gas chromatograph for the analysis of natural gas consists of the sequential steps given in 6.2 to 6.9, choosing the appropriate option at Step 4 (see 6.5) before the analyser can be put into operation. At Step 4, the setting-up process provides for either the primary multi-point calibration (Type 1 analyses), where the output from the calibration is used in subsequent analyses, or for performance evaluation (Type 2 analyses), which shall be the subject of single-point calibration in normal use and in which the data from the evaluation is required for the calculation composition. The primary calibration and evaluation steps may have to be repeated in subsequent operational use, for example when there is a significant change in the composition of the gas to be analysed which takes it outside the ranges of composition for which the analyser has been calibrated/evaluated.

The complete procedure for determining the mole fraction (and related uncertainty; see ISO 6974-2) of each component in a natural gas mixture is shown schematically in the flowcharts in Figures 1 and 2.

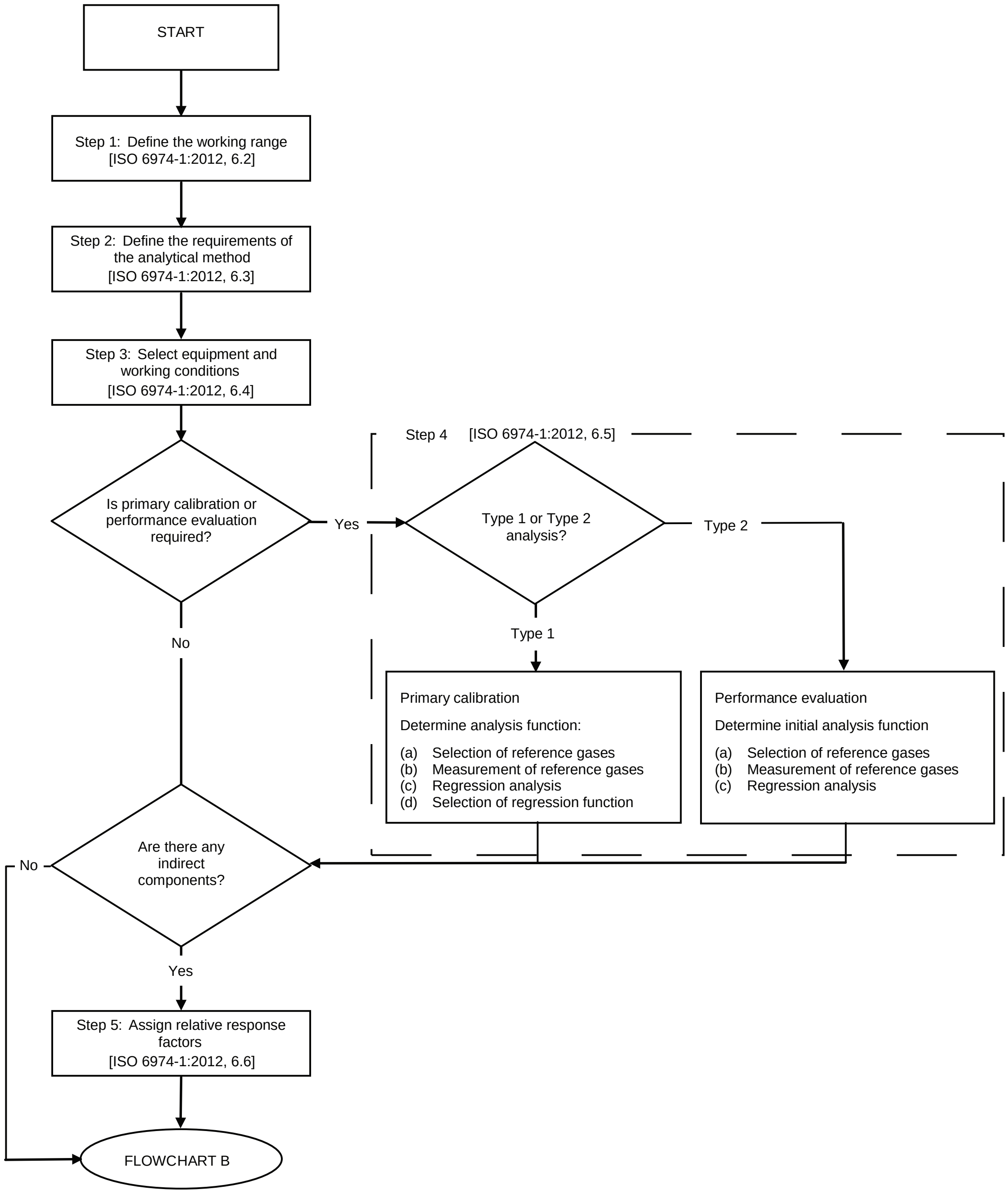

Figure 1 — Procedure for determining mole fraction (and uncertainty in accordance with ISO 6974-2) — Steps 1 to 5

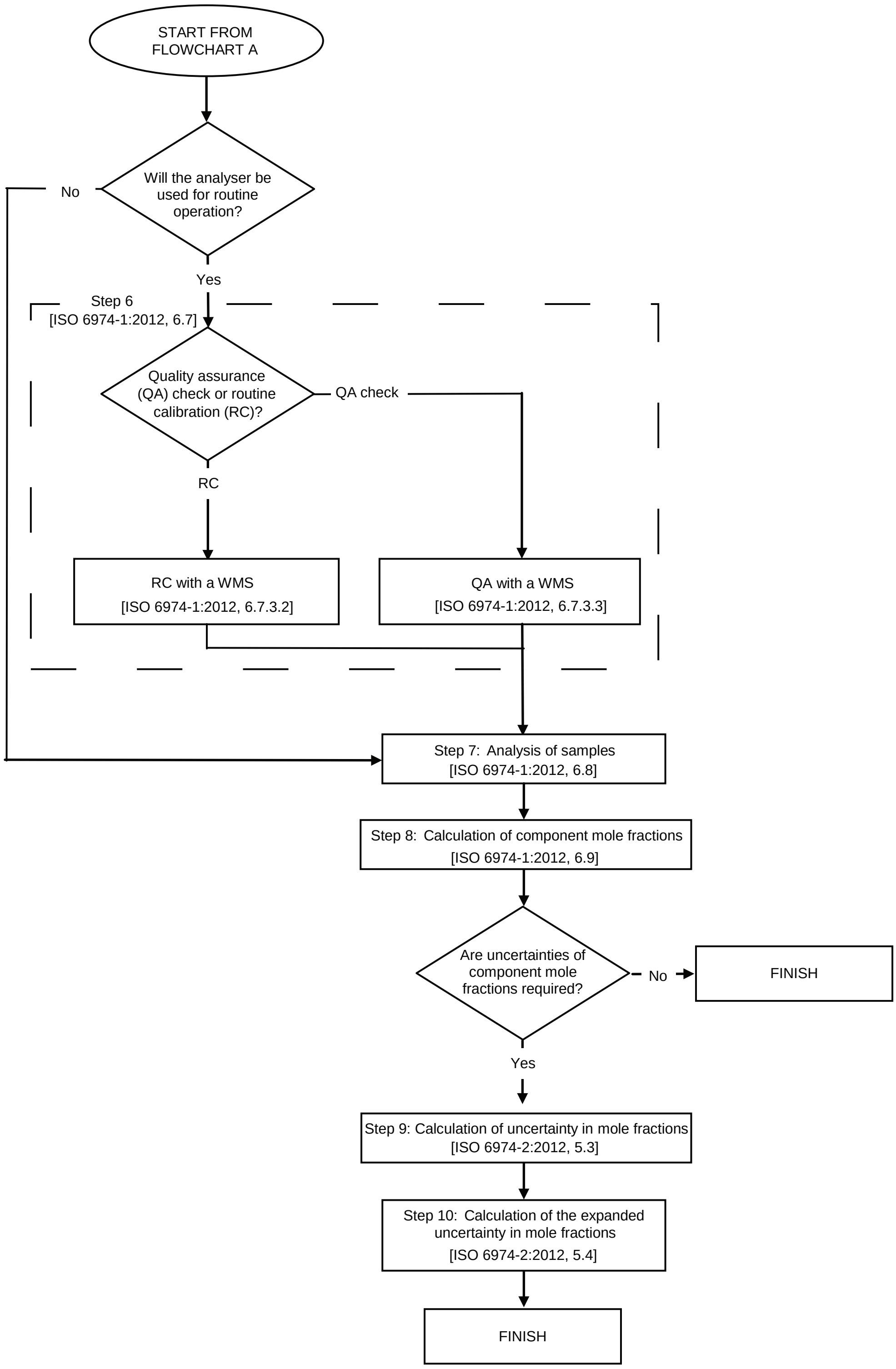

Figure 2 — Procedure for determining mole fraction (and uncertainty in accordance with ISO 6974-2) — Steps 6 to 10

6.2 Step 1 — Defining the working range

6.2.1 Specify the working range for the analyser, giving minimum and maximum mole fractions for all the components to be analysed and estimated mole fractions of any components not analysed. The working range shall be based upon the probable variations in the composition of the gas to be analysed and on the application requirements.

6.2.2 The probable variations in the composition of the gas can be established as follows:

— by evaluating historic data, where this is available;

— by performing extended analyses of a number of representative samples of the gas to be analysed, taking into account possible variations of upstream gas treatment and processing; or

— by reference to a specification of the delivered or supplied product as provided by the network operator.

6.2.3 The working range shall then be determined in relation to the probable variations in the composition of the gas to be analysed, where for each component the following applies:

— the minimum of the working range is no higher than the lowest expected mole fraction;

— the maximum of the working range is no lower than the highest expected mole fraction.

6.2.4 The mole fractions of other components that are not analysed may be estimated from historical data or extended analyses.

6.3 Step 2 — Defining the requirements of the analytical method

Outline the requirements of the analytical method by defining the following aspects:

— components to be measured directly and (where required) the uncertainties, either on individual components or by mole fraction ranges;

— components to be measured indirectly and (where required) the uncertainties, either on individual components or by mole fraction ranges;

— components to be measured as groups and (where required) the uncertainties;

— components not to be measured but for which a constant value is to be used for their mole fractions;

— whether to use bridge components for multiple operation methods [and, if so, selecting which component(s) are to be used as bridge components];

— whether to carry out backflush or not; and

— any interfering components.

NOTE Typical uncertainties of the analysis result for various configurations of laboratory and on-line measuring systems can be found in ISO 6974-3 and subsequent parts of ISO 6974.

6.4 Step 3 — Selecting equipment and working conditions

Select the equipment and working conditions required. ISO 6974-3 and subsequent parts of ISO 6974 prescribe methods of analysis that are intended to be used in conjunction with this part of ISO 6974. Other methods, if properly documented, may be used in place of ISO 6974-3 and subsequent parts.

Select the method of sample handling and injection:

— the natural gas sample is contained within a cylinder that is attached to the chromatograph gas sampling valve; or

— the natural gas is continuously sampled from a pipeline and flows through the chromatograph gas sampling valve, which is used to inject a representative sample into the chromatograph.

Detailed guidelines on sampling are given in ISO 10715[7].

NOTE Special attention needs to be given to prevent condensation of heavier components when the sample pressure is reduced — see ISO 16664[8] for detailed information on the handling of calibration gases and gas mixtures.

If a primary calibration or performance evaluation is not required, and if the analyser will be used for routine operation, proceed to a quality assurance (QA) check or routine calibration [see Step 6 (6.7)].

If a primary calibration or performance evaluation is not required, and if the analyser will only be used for a single analysis, proceed to the analysis of the unknown mixtures [see Step 7 (6.8)].

6.5 Step 4 — Response characteristics (primary calibration or performance evaluation)

6.5.1 General considerations

For Type 1 analyses, determination of response characteristics takes the form of a primary calibration in which the coefficients $b_{z,i}$ of the analysis function are determined for each component. Because the analysis function is determined explicitly, no non-linearity errors arise. For routine operation, the coefficients of the analysis function are subsequently corrected by multiplying by a scaling factor [see Step 6 (6.7)].

For Type 2 analyses, determination of the analysis function of the analyser is assumed to be first order with a zero intercept (i.e. b_0, b_2 and b_3 are zero), and this assumed analysis function is subsequently updated periodically by analysis of the WMS [see Step 6 (6.7)]. The assumption of a first-order response with zero intercept for the analysis function can lead to non-linearity errors, and the purpose of the performance evaluation is to estimate their magnitude in order to assess fitness for purpose and, if required, to enable the correction of calculated mole fractions (see 6.9.4). If the uncertainty of mole fractions is calculated using ISO 6974-2, these non-linearity errors may be included in the uncertainty budget.

6.5.2 Frequency

Primary calibration or performance evaluation should be carried out in the following situations:

- immediately following initial installation of the system by the supplier;
- immediately following return to operation after replacement of a major part of the system, e.g. injection valve, column or detector;
- immediately following return to operation after failure to pass a QA check of the system [see Step 6 (6.7)];
- at intervals that have been demonstrated to be appropriate for the application, e.g. no longer than 12 months.

6.5.3 Selecting reference gases

An appropriate number of CRMs shall be selected in order to define the regression functions. This depends upon the history and knowledge of the GC system in question:

- where no primary calibration has been carried out, or the response polynomials have not been established by an equivalent procedure, then a minimum of seven CRMs should be selected to allow for regression curves that are up to third order in nature;
- where the initial primary calibration (or an equivalent procedure) has shown that regression curves can be modelled by a first- or second-order polynomial function, then an appropriate number of CRMs should be selected for subsequent primary calibrations.

“An appropriate number” of CRMs may be considered to be three in incidences where no component demonstrates more than a first-order polynomial response, and five in incidences where no component demonstrates more than a second-order polynomial response.

Choose CRMs suitable for the working range of each component (as defined in 6.2). This is possible by using a set of multi-component mixtures, each containing different mole fractions of all the direct components.

The CRMs selected may be multi-component or binary mixtures with appropriate uncertainty and should always be fit for purpose (see ISO 6143 and ISO 6142[9]), i.e. the uncertainty of each component should be small enough that it gives an acceptably small final uncertainty after propagation through the full uncertainty budget.

NOTE It is not possible to make a mixture with every component at the highest level required, or at the lowest, so most of the multi-component CRMs will have compositions that are different from “real” natural gas mixtures. Provided the mixtures are shown to be stable in storage and use, this will not create a problem.

CRMs are generally provided with expanded uncertainties calculated with a coverage factor, k, normally equal to 2. A coverage factor of 2 should therefore be used as the default option in the absence of any other evidence.

6.5.4 Measuring reference gases

Analyse each of the CRMs. It is recommended that a minimum of 10 analyses be performed for each reference gas so as to ensure that the mean response data and their standard uncertainties are determined with a precision that is fit for purpose.

NOTE The uncertainties referred to in this subclause are not used in this part of ISO 6974, but are required if ISO 6974-2 is to be used to determine uncertainties of mole fractions.

Depending on the number of repeated measurements, the “uncertainty of the uncertainty” of a mean value (i.e. the relative standard deviation of the standard deviation of a mean value) can be surprisingly large: for 10 measurements it is 24 % (see ISO/IEC Guide 98-3:2008, E.4.3). It is therefore not recommended to use a smaller number of repeated measurements when determining the standard deviation of a mean value.

Tabulate the individual responses to each component in each standard for each replicate. The data may be inspected for outliers by using a suitable outlier test (see Annex E). If outliers are found, the data should be investigated; outliers should be rejected only if there are sound technical reasons for doing so.

6.5.5 Regression analysis

6.5.5.1 Introduction to regression analysis

It is strongly recommended that generalized least squares (GLS) analysis be undertaken. GLS analysis, which complies with ISO 6143, requires that the uncertainties of the input data be determined and performs regression weighted to these uncertainties. The value of each component mole fraction is calculated, along with its uncertainty. GLS shall therefore be used if ISO 6974-2 will subsequently be used to determine the uncertainty of mole fractions.

For cases where the uncertainties of component mole fractions (and therefore compliance with ISO 6974-2) are not required, either GLS analysis with zero (or negligibly small) input uncertainties or ordinary least squares (OLS) analysis may be used. However, even when the uncertainties of component mole fractions are not required, it is recommended that GLS be used with defined input uncertainties whenever possible. This gives the most reliable determination of component mole fractions.

6.5.5.2 Generalized least squares analysis

The analysis function (primary calibration) is given in Equation (2):

$$x^*_i = b_0 + b_1 y_i + b_2 y_i^2 + b_3 y_i^3 \qquad (2)$$

The calibration function (performance evaluation) is given in Equation (3):

$$y_i = a_0 + a_1 x_{\text{cert},i} + a_2 x_{\text{cert},i}^2 + a_3 x_{\text{cert},i}^3 \qquad (3)$$

The coefficients of the analysis function or the calibration function are calculated using regression analysis of the following input data:

— the CRM contents (expressed as certified mole fractions), x_{cert};

- the standard uncertainties of the CRM contents, $u(x_{\text{cert},i})$ (required where uncertainties are to be calculated in accordance with ISO 6974-2);
- the mean responses to the CRM contents, $\bar{y}_{\text{cert},i}$;
- the standard uncertainties of the mean responses, $u(\bar{y}_{\text{cert},i})$, calculated as the standard error of the mean of the set of responses obtained (required where uncertainties are to be calculated in accordance with ISO 6974-2).

If atmospheric pressure correction is to be carried out, the responses shall be corrected prior to regression analysis, by applying the appropriate pressure correction factor. Annex F gives guidance on correction for atmospheric pressure.

If a multiple operation method with bridging (see 5.2.2) is used, the mean response to the analyte contents is calculated, for each appropriate component, as the mean of the responses derived from the second or subsequent detector, multiplied by the ratio of the response obtained for the bridge component with the first detector to that obtained with the second or subsequent detector, as given in Equation (4):

$$\bar{y}_i = \bar{y}_{\text{d2},i} \times \frac{y_{\text{d1,bc}}}{y_{\text{d2,bc}}} \tag{4}$$

If required, the standard uncertainties of the mean responses derived using Equation (4) are calculated as the standard error of the mean of the derived data set.

The parameters of the regression function are then calculated by regression analysis. For the reasons described in 6.5.5.1, it is strongly recommended that GLS be used. Software appropriate for carrying out such an analysis is described in Annex G.

In a small number of specific circumstances, the acceptable levels of uncertainty may be relatively large. In these cases, the uncertainty of raw components may be evaluated using an OLS method. The uncertainty arising from the regression analysis shall be in accordance with ISO/IEC Guide 98-3. One such approach, which relies on knowledge of the uncertainties inherent in the CRMs, the analysis and the gradient in the calibration curve, is outlined in Annex H.

For cases where the uncertainties of component mole fractions (and therefore compliance with ISO 6974-2) are not required, either GLS analysis with zero (or negligibly small) input uncertainties or ordinary least squares (OLS) analysis may be used. However, even when the uncertainties of component mole fractions are not required, it is recommended that GLS be used with defined input uncertainties whenever possible. This gives the most reliable determination of component mole fractions.

6.5.5.3 Ordinary least squares analysis

For ordinary least squares analysis, only the input parameters $x_{\text{cert},i}$ and $y_{\text{cert},i}$ defined in 6.5.5.2 need to be determined. If required, atmospheric pressure correction and/or bridging shall be performed as described in 6.5.5.2.

Software appropriate for performing OLS analysis is widely available.

6.5.6 Selecting the regression functions

Polynomial functions shall be used in regression analysis and the coefficients shall be determined by following the procedure outlined in ISO 6143 (if using GLS) or using suitable software (if using OLS).

NOTE 1 This subclause applies to use of GLS to determine regression functions. For OLS methods, a statistical test, for example a sequential F-test[10], can be used to determine the appropriate order of the polynomial function.

The order of polynomial for each component shall be chosen with the following assumptions in mind:

- the simplest function that gives an adequate fit to the data should be used to avoid describing the instrumental response through an unnecessarily complicated function;
- the minimum number of calibration points recommended for the different types of functions considered are three for a first-order function, five for a second order and seven for a third order;

— curvature of the regression function can be described by a second- (and possibly third-) order term. If none of these functions are suitable, it may indicate a problem with the method or equipment;

— the presence of a maximum or a minimum in the plot of calculated mole fractions versus response within the working range indicates a problem.

Functions of second and higher orders should be used with caution. In general, the chromatographic detectors used in natural gas analysis (TCD and FID) have linear response characteristics. Non-linear responses are most commonly observed for methane (caused by detector overload due to the very large mole fraction) or for other species near their limits of detection.

NOTE 2 The use of a single CRM for the primary calibration of the instrument will not enable the identification of the correct form for the regression function. The use of this approach is therefore outside the scope of this part of ISO 6974.

A satisfactory fit is required for the ith component at each individual calibration point by using the following test procedure. For each experimental calibration point (x_i, y_i), an adjusted calibration point $(\hat{x}_i, \hat{y}_i)$ is calculated, as a by-product of the regression analysis used to determine the regression function. The coordinates $\hat{x}_i$ and $\hat{y}_i$ of the adjusted calibration point are estimates of the true analyte content of, and the true response to, the reference gas. By construction, the calculated response curve passes through the adjusted calibration points. The selected response model is considered compatible with the calibration data set if the following conditions are fulfilled for every calibration point ($l = 1, 2, ..., n_l$):

$$\left|\hat{x}_{i,l} - x_{i,l}\right| \le ku(x_{i,l}) \text{ and } \left|\hat{y}_{i,l} - y_{i,l}\right| \le ku(y_{i,l})$$

NOTE 3 In almost all cases, this condition is equivalent to requiring that the calculated response curve pass through every experimental “calibration rectangle”, $\left[x_{i,l} \pm ku\left(x_{i,l}\right), y_{i,l} \pm ku\left(y_{i,l}\right)\right]$, based on the expanded uncertainty $U = ku$. A coverage factor of $k = 2$ is used for this test.

If the model validation test fails, one possibility is to examine other response models until a model is found that is compatible with the calibration data set. Another possibility is to examine, and possibly revise, the calibration data.

To test effectively the compatibility of a prospective regression function, calculate the measure of goodness-of-fit, Γ, defined as a maximum value of the following weighted differences between the coordinates of measured and adjusted calibration points ($l = 1, 2, …, n_l$):

$$\left|\hat{x}_{i,l} - x_{i,l}\right| / u(x_{i,l}) \text{ and } \left|\hat{y}_{i,l} - y_{i,l}\right| / u(y_{i,l})$$

A function is admissible if $\Gamma \le 2$.

If several functions are considered and found to be admissible, the function with the fewest parameters should be chosen for use.

Each calculated response curve should be inspected visually. This visual inspection is necessary to reveal “nonsense correlations”, which can occur without being detected by local examination of the curve fit to the calibration points. Such nonsense correlations are liable to occur with polynomial response functions, which can exhibit non-monotonic behaviour with excellent local fit. Another case of nonsense correlations can occur if, by mistake, one of the calibration data uncertainties is very small. This calibration point is then erroneously given a very high weight. Consequently, the response curve is forced through this point with little importance given to the other calibration points.

6.6 Step 5 — Relative response factors

Where no components are measured indirectly, this step is omitted from the set-up of the analyser.

The relative response factors for groups of components which are measured indirectly are given in Annex D. Where a group of components, for example C_{6+}, are measured indirectly, extended analysis of a typical sample shall be used to quantify the total amount of C_{6+} and also the reference component, e.g. propane or *n*-butane.

Subsequent comparison of the area of the reference component and the determined response of the group of components allows the relative response factor to be calculated.

NOTE 1 The use of a relative response factor (which has an inherent uncertainty) increases the uncertainty of the measured mole fraction.

NOTE 2 Using the relative response factor of the "normal" C_n isomer for the C_{n+} fraction, where n indicates the number of carbon atoms, can introduce significant systematic error.

6.7 Step 6 — Routine calibration/quality assurance check

6.7.1 General considerations

Routine calibration employs periodic injection of a working measurement standard (WMS) in order to either correct the coefficients of the analysis functions (Type 1 analyses) or to update the coefficients $b_{1,i}$ of the assumed analysis functions (Type 2 analyses).

NOTE 1 The WMS can be of a different composition to the CRM(s) used in Step 4 (see 6.5).

Quality assurance checking employs periodic injection of a WMS to determine the stability of the measuring system over time according to the guidelines presented in Clause 7. Appropriate action shall be taken to re-establish values for coefficients if the performance of the system fails to meet the established requirements.

For routine operation of Type 1 analyses, the coefficients of the analysis function (determined in Step 4; see 6.5) are subsequently corrected by applying a scaling factor. The scaling factor is the response to the WMS obtained immediately after primary calibration, divided by its current value, as given in Equation (5):

$$b'_{z,i} = b_{z,i} \frac{y_{\mathrm{o},i,\mathrm{wms}}}{y_{i,\mathrm{wms}}} \tag{5}$$

Equation (5) describes a commonly-used approach for correcting the coefficients of an analysis function. Other approaches for correction may be used, but only if the user can justify that they are more fit for purpose for their instrument.

During Type 2 analyses, the analysis function of the analyser is assumed to be first order with zero intercept (i.e. b_0, b_2 and b_3 are zero) and this assumed analysis function is subsequently updated periodically by routine calibration (i.e. analysis of the WMS). See Equation (6):

$$b_{1,i} = \frac{x_{i,\mathrm{wms}}}{y_{i,\mathrm{wms}}} \tag{6}$$

NOTE 2 $b_{1,i}$ is the reciprocal of the "response factor".

6.7.2 Frequency

The routine calibration or quality assurance interval depends mainly on the measurement system and the measuring circumstances. It is therefore not possible to give a general value, but the interval should be determined using either of the following procedures:

- Where no nominal routine calibration/quality assurance interval has been set, the system shall be calibrated and then tested, without further calibration or adjustment, until such time as the performance of the system fails to meet requirements. Once the interval to failure has been established, a period shorter than this shall be selected as the routine calibration/quality assurance interval.
- Where a nominal routine calibration/quality assurance interval has been set, the system shall be calibrated and then tested, without further calibration or adjustment, until the nominal routine calibration/quality assurance interval has been exceeded. Provided the performance of the system has met requirements, the nominal interval may be selected for use. If the performance of the system has failed to meet requirements over the nominal routine calibration/quality assurance interval, then a shorter period, over which the requirements were met, shall be selected as the routine calibration/quality assurance interval.

In practice, the intervals between routine calibrations or quality assurance checks are likely to range from less than one week to one year.

6.7.3 Procedure

6.7.3.1 General considerations

Carry out the required number of injections of samples of the WMS. If atmospheric pressure correction is carried out, correct the mean responses by applying the pressure correction factor (see Annex F). Determine the mean response of the analyser to each component.

6.7.3.2 Routine calibration

For Type 1 analyses, the coefficients of the analysis function for each component — obtained at primary calibration — are corrected by multiplying them by the ratio of the current mean response to the WMS to the mean obtained at primary calibration.

For Type 2 analyses, the coefficient of the assumed analysis function is updated.

6.7.3.3 Quality assurance checks

Carry out a quality assurance check using a recognized control chart procedure. Guidance on quality assurance checks is given in Annex H.

6.8 Step 7 — Analysis of samples

The manner of carrying out the analysis of natural gas mixtures will depend on the way in which the mixture is sampled and presented to the analyser.

Where the natural gas mixture is sampled into a cylinder and gas samples are then taken from the cylinder and injected into the analyser, it is recommended that 10 analyses be carried out (see the comments on the number of replicate analyses in 6.5.4). If the analyser is operated under statistical control, then it is permitted to carry out fewer analyses, and estimates of the uncertainty evaluated from prior statistical data may be used. Laboratory analysers are generally operated in this manner.

Where the natural gas sample presented to the analyser has been taken from a source where the composition of the gas may change with time (for example from a natural-gas pipeline), or when the quantity of sample is small, then it will not be possible to carry out repeat analyses of the gas sample. In this case, the analyser shall be operated under statistical control and the standard deviation predetermined in order to be able to calculate the uncertainties of the component mole fractions. Field analysers are generally operated in this way.

NOTE For this latter case (where repeat analyses are not possible), the two methods discussed in Step 8 (6.9) — the mean normalization method and the run-by-run normalization method — converge. Equations (7) and (16) (which calculate of the means of the mole fractions) then become identical. If calculating the uncertainty of mole fractions, Equations (5) and (16) in ISO 6974-2:2012 also become identical.

It is recommended that the required standard deviation data be obtained from the primary calibration data. However, as standard deviation is closely related to mole fraction, it can be acceptable to obtain the standard deviation from repeated analyses of the WMS (used during statistical control purposes) provided the composition of the WMS is close to that of the gas under analysis.

6.9 Step 8 — Calculation of component mole fractions

6.9.1 General considerations

There are a number of possible methods for treating the $y_{i,l}$ data that can be employed to generate mole fractions. The two most common methods employed are given below.

a) Mean normalization: The repeat analyses for each component are averaged to form a series mean and then normalized. Treatment of data using this method is described in 6.9.2.

b) Run-by-run normalization: Each repeat analysis is normalized independently; the average of these normalized values is then calculated. Treatment of data using this method is described in 6.9.3 and leads to the values of y_i for each analysis.

NOTE Normalization makes use of pressure correction, i.e. the correction of mean responses to the sample for variation in atmospheric pressure (see Annex F), unnecessary.

6.9.2 Calculation of component mole fractions using the mean normalization method

6.9.2.1 Single operation methods or multiple operation methods without bridging

Calculate the mean responses to n_l injections of the sample using Equation (7):

$$\overline{y_i} = \frac{\sum\limits_{l=1}^{l=n_l} y_{i,l}}{n_l} \qquad (7)$$

6.9.2.2 Multiple operation methods with bridging

If a multiple operation method with bridging (see 5.2.2) is used, the response to the analyte contents is calculated, for each appropriate component, as the response derived from the second or subsequent detector multiplied by the ratio of the response obtained for the bridge component using the first detector to that obtained using the second or subsequent detector, as given in Equation (8):

$$y_i = y_{\mathrm{d2},i} \times \frac{y_{\mathrm{d1,bc}}}{y_{\mathrm{d2,bc}}} \qquad (8)$$

6.9.2.3 Calculation of raw mole fractions

Calculate the raw mole fractions from the mean responses and either the calibration function (Type 1 analyses) or the assumed calibration function (Type 2 analyses), using Equation (9):

$$x_i^* = \overline{b_{0,i}} + \overline{b_{1,i} y_i} + \overline{b_{2,i} y_i}^2 + \overline{b_{3,i} y_i}^3 \qquad (9)$$

The terms in the calibration function $b_{z,i}$ are estimates of $\overline{b_{z,i}}$. For Type 2 analyses, terms in b_0, b_2 and b_3 are zero.

If routine calibration is practised, then the latest corrected values of the coefficients of the analysis function (Type 1 analyses) or the latest updated response factor (Type 2 analyses) shall be employed [see Step 6 (6.7)].

6.9.2.4 Indirect components

For all single and multiple operation methods, calculate the raw mole fractions of the indirect components in the sample using Equation (10):

$$x^{*}_{\mathrm{ind},i} = K_i \times \frac{\overline{y}_{\mathrm{ind},i}}{\overline{y}_{\mathrm{ref}}} \times x^{*}_{\mathrm{ref}} \qquad (10)$$

The relative response factors, K_i, for flame ionization detectors (FIDs) and thermal conductivity detectors (TCDs) are given in Annex D. The measurement of indirect components is valid only when the uncertainties inherent in the relative response factors are evaluated correctly.

6.9.2.5 Normalization

Calculate the normalized mole fractions using Equation (11):

$$x_i = \left(1 - x_{\mathrm{oc}}\right) \frac{x^{*}_i}{T} \qquad (11)$$

where, for single operation methods or multiple operation methods without bridging:

$$T = \sum_{i=1}^{n_i} x^{*}_i$$

or, for multiple operation methods with bridging:

$$T = \sum_{i=1}^{\mathrm{bc}_1} x^{*}_i + \sum_{i=\mathrm{bc}_1+1}^{\mathrm{bc}_2} x^{*}_i + \ldots + \sum_{i=\mathrm{bc}_m+1}^{n_i} x^{*}_i$$

where m is the number of bridge components (bc_1, bc_2, … bc_m).

6.9.3 Calculation of component mole fractions using the run-by-run normalization method

6.9.3.1 General considerations

The procedure for calculating the component mole fractions using the run-by-run normalization method is described in 6.9.3.2 to 6.9.3.6.

6.9.3.2 Multiple operation methods with bridging

If a multiple operation method with bridging (see 5.2.2) is used, the response to the analyte contents is calculated, for each appropriate component, as the response derived from the second or subsequent detector multiplied by the ratio of the response obtained for the bridge component using the first detector to that obtained using the second or subsequent detector:

$$y_{i,l} = y_{\mathrm{d2},i,l} \times \frac{y_{\mathrm{d1,bc},l}}{y_{\mathrm{d2,bc},l}} \qquad (12)$$

6.9.3.3 Calculation of raw mole fractions

Calculate the raw mole fractions for a series of injections of unknown sample, using either the calibration function (Type 1 analyses) or the assumed calibration function (Type 2 analyses), in accordance with Equation (13):

$$x_{i,l}^{*} = b_{0,i} + b_{1,i} y_{i,l} + b_{2,i}\left(y_{i,l}\right)^{2} + b_{3,i}\left(y_{i,l}\right)^{3} \tag{13}$$

The terms of the calibration function $b_{z,i}$ are estimates of $b_{z,i,l}$. For Type 2 analyses, the terms b_0, b_2 and b_3 are equal to zero.

If routine calibration is practised, then the latest corrected values of the coefficients of the analysis function (Type 1 analyses) or the latest updated response factor (Type 2 analyses) shall be employed [see Step 6 (6.7)].

6.9.3.4 Indirect components

For all single and multiple operation methods, calculate the raw mole fractions of the indirect components in the sample using Equation (14):

$$x_{\text{ind},i,l}^{*} = K_i \times \frac{y_{\text{ind},i,l}}{y_{\text{ref},l}} \times x_{\text{ref},l}^{*} \tag{14}$$

The relative response factors, K_i, for FIDs and TCDs are given in Annex D. The measurement of indirect components is only valid when the uncertainties inherent in the relative response factors are evaluated correctly.

6.9.3.5 Normalization

Calculate the normalized mole fractions using Equation (15):

$$x_{i,l} = \left(1 - x_{\text{oc}}\right)\frac{x_{i,l}^{*}}{T_l} \tag{15}$$

where

$$T_l = \sum_{i=1}^{n_i} x_{i,l}^{*}$$

for single operation methods or multiple operation methods without bridging, or

$$T_l = \sum_{i=1}^{\text{bc}_1} x_{i,l}^{*} + \sum_{i=\text{bc}_1+1}^{\text{bc}_2} x_{i,l}^{*} + \ldots + \sum_{i=\text{bc}_m+1}^{n_i} x_{i,l}^{*}$$

for multiple operation methods with bridging for m bridge components (bc_1, bc_2, … bc_m).

6.9.3.6 Calculation of the means of the mole fractions

Calculate the mean of the normalized mole fractions using Equation (16):

$$\overline{x_i} = \frac{\sum_{l=1}^{l=n_l} x_{i,l}}{n_l} \tag{16}$$

6.9.4 Non-linearity errors (Type 2 analyses)

In Type 2 analyses, non-linearity errors may arise because of a difference between the true and assumed response of the analyser. Such non-linearity errors are dependent upon the composition of the WMS, the composition of the unknown sample and the form of the true response (i.e. the calibration function, as determined by performance evaluation).

Non-linearity errors may be determined by analysing two or more CRMs of appropriately chosen composition or by calculating, for a series of hypothetical compositions, the composition of the WMS and the calibration function determined during performance evaluation.

Ideally, the analyser should be set up so as to ensure that the mean, $\overline{\delta_i}$, of the distribution of non-linearity errors $\delta\left(x_i^*\right)$ determined over the analytical range of the analyser is close to zero. In such circumstances, no correction should be applied. If uncertainties in component mole fractions are required, the correction factor is included as an additional term in the uncertainty budget; see ISO 6974-2:2012, Equations (3) and (14).

Non-linearity errors are corrected by determining the distribution of non-linearity errors for a range of hypothetical compositions corresponding to the analytical range of the instrument. Calculate the mean non-linearity error for the distribution and, if not close to zero, apply a correction factor as given by Equation (17) when using the mean normalization method or Equation (18) when using the run-by-run normalization method:

$$x_{i,\text{corr}}^* = x_i^* - \overline{\delta_i} \tag{17}$$

$$x_{i,l,\text{corr}}^* = x_{i,l}^* - \overline{\delta_i} \tag{18}$$

The value of $\overline{\delta_i}$ will depend on the extent to which the true analysis function of the analyser deviates from the assumed linear response with zero intercept, the analysis range of the instrument, and the composition chosen for the WMS used in routine calibration.

NOTE ISO 6974-2 uses x_i^* and $x_{i,l}^*$ as generic symbols for raw mole fractions, irrespective of whether the mole fraction has been corrected for non-linearity errors.

7 Control chart

Control charts should be used for determining whether the system is working satisfactorily. The use of control charts is described in Annex H.

8 Test report

The test report shall include the following information:

a) identification of the sample, including
  - time and date of sampling (if available),
  - sample point (location) (if available), and
  - identification number for the cylinder (or vessel) used for the sample;

b) information on the gas chromatographic method used, including
  - a reference to the appropriate part(s) of ISO 6974 or other documented methods, and
  - any significant deviations from the referenced method;

c) analytical information, including
  - result of the analysis, expressed as a mole fraction,
  - for analyses where ISO 6974-2 has been used, the expanded uncertainty of the analytical value (stating the coverage factor, *k*, used to expand the uncertainty; *k* will usually be 2),

- date of the analysis, and
- information about any corrections made for contamination by air or other gases, if appropriate;

d) laboratory information, including

- date of issuance of the report,
- name and address of the laboratory, and
- signature of the authorized signatory.

NOTE The results of analysis carried out using ISO 6974 can be used in conjunction with additional information for the certification of a CRM.

Annex A
(informative)

Comparative application ranges and characteristics of analytical methods described in ISO 6974-3 to ISO 6974-6

Table A.1 — Application ranges of analytical methods described in ISO 6974-3 to ISO 6974-6

Components measured	Mole fraction range %			
	ISO 6974-3	ISO 6974-4	ISO 6974-5	ISO 6974-6[a]
Helium	0,01 to 0,5	—	—	0,002 to 0,5
Hydrogen	0,01 to 0,5	—	—	0,001 to 0,5
Oxygen	0,1 to 0,5	—	—	0,007 to 5
Nitrogen	0,1 to 40	0,001 to 15	0,1 to 22	0,007 to 40
Carbon dioxide	0,1 to 30	0,001 to 10	0,05 to 15	0,001 to 10
Methane	50 to 100	75 to 100	34 to 100	40 to 100
Ethane	0,1 to 15	0,001 to 10	0,1 to 35	0,002 to 0,5
Propane	0,001 to 5	0,001 to 3	0,05 to 10	0,001 to 5
iso-Butane	0,000 1 to 2	0,001 to 1	0,01 to 2	0,000 1 to 1
n-Butane	0,000 1 to 2	0,001 to 1	0,01 to 2	0,000 1 to 1
neo-Pentane	0,000 1 to 1	0,001 to 0,5	0,005 to 0,35	0,000 1 to 0,5
iso-Pentane	0,000 1 to 1	0,001 to 0,5	0,005 to 0,35	0,000 1 to 0,5
n-Pentane	0,000 1 to 1	0,001 to 0,5	0,005 to 0,35	0,000 1 to 0,5
Hexanes+	—	0,001 to 0,2	0,005 to 0,35	—
Total C6	0,000 1 to 0,5	—	—	0,000 1 to 0,5
Total C7	0,000 1 to 0,5	—	—	0,000 1 to 0,5
Total C8	0,000 1 to 0,5	—	—	0,000 1 to 0,5

[a] ISO 6974-6 also gives application ranges for carbon monoxide, ethyne, ethene, propene, cyclopentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, benzene, cyclohexane, methylcyclohexane, toluene and xylenes.

Table A.2 — Chromatographic conditions of analytical methods described in ISO 6974-3 to ISO 6974-6

Conditions	ISO 6974-3	ISO 6974-4	ISO 6974-5	ISO 6974-6
No. of columns	2	2	3	3
Column temperature	a) 35 °C to 200 °C at 15 °C/min b) 30 °C to 250 °C at 30 °C/min	Isothermal	Isothermal	a) 30 °C to 120 °C at 12 °C/min b) 35 °C to 240 °C at 8 °C/min
Carrier gas	a) Helium b) Argon	Helium	Helium	a) Argon b) Nitrogen
Detectors	a) TCD and FID b) TCD	TCD	TCD	a) TCD and FID b) FID
Column switching	No	Yes	Yes	Yes
Analysis time	a) 44 min b) 24 min	≤ 20 min	4 min to 7 min	a) 43 min b) 40 min
Cycle time	60 min	≤ 20 min	4 min to 7 min	55 min

NOTE The indications (a) and (b) refer to distinct parts of the analytical method.

Annex B
(informative)

Alternative approach to bridging and normalization

B.1 General considerations

This annex describes the procedure for calculating mole fractions and associated uncertainties for analyses with the run-by-run or mean normalization method, using the generalized least squares (GLS) method or Lagrange multipliers. Analysis of a gas sample results in the measured values $x_{i,l}^{*}$, as described by the flowchart in Figure B.1. An overview of the data conversions is given in Figure B.2.

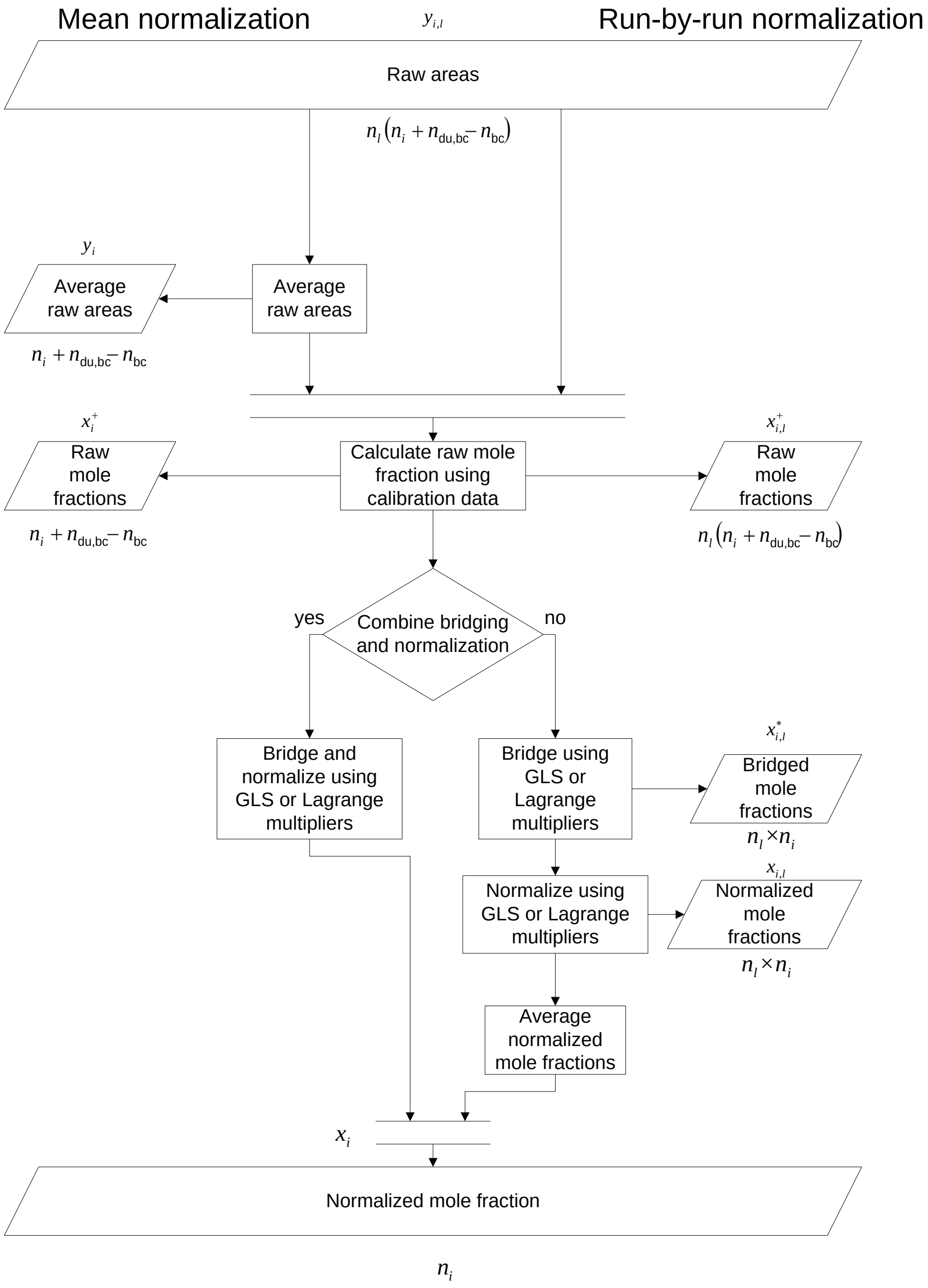

Figure B.1 — Calculation of normalized mole fraction using mean normalization or run-by-run normalization

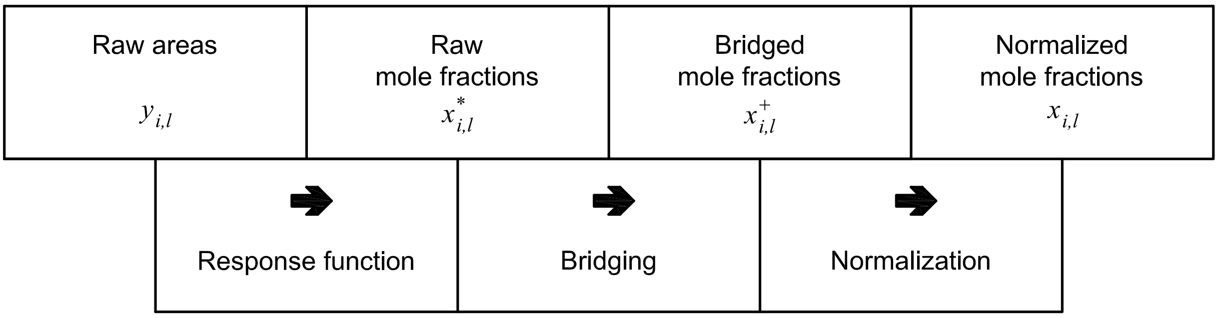

Figure B.2 — Overview of data conversion process

Subclauses 5.2.2, 5.2.3 and 5.5 describe, respectively, the procedure for converting $x^{+}_{i,l}$ to $x^{*}_{i,l}$, the case in which $x^{+}_{i,l}$ and $x^{*}_{i,l}$ are identical, and the procedure for converting $x^{*}_{i,l}$ to $x_{i,l}$. However, the methods described in these subclauses can only be used under certain conditions; these are described in more detail in B.2. Under different conditions, alternative calculation models can be used, for example GLS or Lagrange multipliers.

The text below describes three examples in detail: bridging, normalization, and bridging with normalization for the run-by-run normalization method. For the mean normalization method, l can be considered equal to unity. The matrix $\boldsymbol{Y}$, as described in B.2.6, then has only one row that contains an averaged mole fraction for the l runs.

Performing only bridging, as described below, can be derived from the most general case, i.e. where Equation (B.1) applies:

$$n_i = n_{\mathrm{bc}} \tag{B.1}$$

Performing only normalization can be derived from the most general case where Equation (B.2) applies:

$$n_{\mathrm{du,bc}} = n_{\mathrm{bc}} = 0 \tag{B.2}$$

B.2 Bridging — Normalization

B.2.1 General considerations

The calculation of the mole fractions and their associated uncertainties can best be described using matrices. The following matrices are defined:

— $\boldsymbol{\Sigma}$: the variance-covariance matrix of the input data (not necessarily of all raw mole fractions);

— $\boldsymbol{B}$: a matrix that contains the constraints;

— $\boldsymbol{A}$: an intermediate matrix that is constructed from $\boldsymbol{\Sigma}$ and $\boldsymbol{B}$;

— $\boldsymbol{D}$: an intermediate matrix;

— $\boldsymbol{Y}$: a matrix that takes into account the raw mole fractions of all analyses;

— $\boldsymbol{H}$: an intermediate matrix that is constructed from $\boldsymbol{Y}$, $\boldsymbol{D}$ and $\boldsymbol{\Sigma}$;

— $\boldsymbol{Z}$: a matrix that contains the results of the calculation (bridged, normalized, or bridged and normalized mole fractions).

The method that can be applied is identical for all types of calculations, whether bridging, normalization, or bridging and normalization, as well as for GLS or Lagrange multipliers. The differences are in the variance-covariance matrix used in the calculations and the auxiliary matrix $\boldsymbol{B}$ that contains the constraints.

B.2.2 Construction of Σ

Matrix $\boldsymbol{\Sigma}$ is the variance-covariance matrix of the relevant components of the analysis. Three different cases can be distinguished: bridging [Equation (B.3)], normalization [Equation (B.4)], and bridging and normalization [Equation (B.5)].

$$\boldsymbol{\Sigma}_{\text{br}} = \begin{bmatrix} \boldsymbol{\Sigma}_1 & & 0 \\ & \ddots & \\ 0 & & \boldsymbol{\Sigma}_{n_{\text{bc}}} \end{bmatrix} \quad (n_{\text{du,bc}} \text{ rows and columns}) \tag{B.3}$$

$$\boldsymbol{\Sigma}_{\text{norm}} = \begin{bmatrix} u^2(x_{1,l}^*) & \cdots & u^2(x_{1,l}^*, x_{n_i,l}^*) \\ \vdots & & \vdots \\ u^2(x_{n_i,l}^*, x_{1,l}^*) & \cdots & u^2(x_{n_i,l}^*) \end{bmatrix} \quad (n_i \text{ rows and columns}) \tag{B.4}$$

$$\boldsymbol{\Sigma}_{\text{br\&norm}} = \begin{bmatrix} u^2(x_{1,l}^+) & \cdots & u^2(x_{1,l}^+, x_{n_i+n_{\text{du,bc}}-n_{\text{bc}},l}^+) \\ \vdots & & \vdots \\ u^2(x_{n_i+n_{\text{du,bc}}-n_{\text{bc}},l}^+, x_{1,l}^+) & \cdots & u^2(x_{n_i+n_{\text{du,bc}}-n_{\text{bc}},l}^+) \end{bmatrix} \quad (n_i + n_{\text{du,bc}} - n_{\text{bc}} \text{ rows and columns}) \tag{B.5}$$

where the matrices $\boldsymbol{\Sigma}_i$ are of the form given in Equation (B.6):

$$\boldsymbol{\Sigma}_i = \left\{ \begin{matrix} u^2(x_{1,l}^+) & \cdots & u^2\left[x_{1,l}^+, x_{n_{\text{du}(\text{bc}_i)},l}^+\right] \\ \vdots & & \vdots \\ u^2\left[x_{n_{\text{du}(\text{bc}_i)},l}^+, x_{1,l}^+\right] & \cdots & u^2\left[x_{n_{\text{du}(\text{bc}_i)},l}^+\right] \end{matrix} \right\} \quad [n_{\text{du}(\text{bc}_i)} \text{ rows and columns}] \tag{B.6}$$

Matrices $\boldsymbol{\Sigma}$ can be of the following forms:

a) diagonal;

b) unitary;

c) blocks of unitary matrices on the diagonal, and zeroes elsewhere;

d) other (any other matrix).

When $\boldsymbol{\Sigma}$ is a diagonal matrix [form a)], the GLS method can be simplified to the Lagrange multiplier method. When there are blocks of unitary matrices on the diagonal and zeroes elsewhere [form c)], the GLS method simplifies to the method described in the main body of this part of ISO 6974.

B.2.3 Construction of B

$$\boldsymbol{B}_{\text{br}} = \begin{bmatrix} \boldsymbol{B}_1 & & 0 \\ & \ddots & \\ 0 & & \boldsymbol{B}_{n_{\text{bc}}} \end{bmatrix} \quad (n_{\text{du,bc}} - n_{\text{bc}} \text{ rows, } n_{\text{du,bc}} \text{ columns}) \tag{B.7}$$

$$\boldsymbol{B}_{\text{norm}} = \begin{bmatrix} 1 & \cdots & 1 \end{bmatrix} \quad (1 \text{ row, } n_i \text{ columns}) \tag{B.8}$$

$$\boldsymbol{B}_{\text{br\&norm}} = \begin{bmatrix} \boldsymbol{B}_{\text{br,0}} \\ \boldsymbol{B}_{\text{norm,1}} \end{bmatrix} \qquad (n_{\text{du,bc}} - n_{\text{bc}} + 1 \text{ rows, } n_i + n_{\text{du,bc}} - n_{\text{bc}} \text{ columns}) \tag{B.9}$$

The matrices $\boldsymbol{B}_i$ are of the form shown in Equation (B.10):

$$\boldsymbol{B}_i = \begin{bmatrix} 1 & -1 & 0 & & \cdots & 0 \\ & 0 & & & & \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ & & & & & 0 \\ 1 & 0 & \cdots & & 0 & -1 \end{bmatrix} \qquad [n_{\text{du(bc}_i)} - 1 \text{ rows, } n_{\text{du(bc}_i)} \text{ columns}] \tag{B.10}$$

The matrix $\boldsymbol{B}_{\text{br,0}}$ is similar to $\boldsymbol{B}_{\text{br}}$ but columns of zeroes are added for the non-bridge components. Matrix $\boldsymbol{B}_{\text{norm,1}}$ [see Equation (B.11)] has a “1” for each non-bridge component and for each first occurrence of a bridge component, and “0” elsewhere:

$$\boldsymbol{B}_{\text{norm,1}} = \begin{bmatrix} 1 & 1 & 0 & \cdots & 1 & 0 & 1 \end{bmatrix} \qquad (1 \text{ row and } n_{\text{du,bc}} \text{ columns}) \tag{B.11}$$

B.2.4 Construction of A

Matrix $\boldsymbol{A}$ is constructed from $\boldsymbol{\Sigma}$ and $\boldsymbol{B}$ as shown in Equation (B.12):

$$\boldsymbol{A} = \begin{bmatrix} \boldsymbol{\Sigma} + \boldsymbol{\Sigma}^{-1} & \boldsymbol{B}^T \\ \boldsymbol{B} & 0 \end{bmatrix} \tag{B.12}$$

Matrix $\boldsymbol{A}$ is a square matrix of the following sizes:

— $2n_{\text{du,bc}} - n_{\text{bc}}$ (for bridging);

— $n_i + 1$ (for normalization);

— $n_i + 2n_{\text{du,bc}} - 2n_{\text{bc}} + 1$ (for bridging and normalization).

B.2.5 Construction of D

Matrix $\boldsymbol{D}$ is defined as given in Equations (B.13) to (B.15):

$$\boldsymbol{D}_{\text{br}} = \begin{bmatrix} 0 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & 0 \end{bmatrix} \qquad (n_{\text{du,bc}} - n_{\text{bc}} \text{ rows, } l \text{ columns}) \tag{B.13}$$

$$\boldsymbol{D}_{\text{norm}} = \begin{bmatrix} 1 & \cdots & 1 \end{bmatrix} \qquad (1 \text{ row, } l \text{ columns}) \tag{B.14}$$

$$\boldsymbol{D}_{\text{br\&norm}} = \begin{bmatrix} 0 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & 0 \\ 1 & \cdots & 1 \end{bmatrix} \qquad (n_{\text{du,bc}} - n_{\text{bc}} + 1 \text{ rows, } l \text{ columns}) \tag{B.15}$$

B.2.6 Construction of Y

Matrix $\boldsymbol{Y}$ is defined to take into account the starting mole fractions, as given in Equations (B.16) to (B.18):

$$\boldsymbol{Y}_{\text{br}} = \begin{bmatrix} x^*_{1,1} & \cdots & x^*_{n_{\text{du,bc}},1} \\ \vdots & & \vdots \\ x^*_{1,l} & \cdots & x^*_{n_{\text{du,bc}},l} \end{bmatrix} \qquad (l \text{ rows, } n_{\text{du,bc}} \text{ columns}) \tag{B.16}$$

$$\boldsymbol{Y}_{\text{norm}} = \begin{bmatrix} \overset{*}{x}_{1,1} & \cdots & \overset{*}{x}_{n_i,1} \\ \vdots & & \vdots \\ \overset{*}{x}_{1,l} & \cdots & \overset{*}{x}_{n_i,l} \end{bmatrix} \quad (l \text{ rows, } n_i \text{ columns}) \tag{B.17}$$

$$\boldsymbol{Y}_{\text{br\&norm}} = \begin{bmatrix} \overset{*}{x}_{1,1} & \cdots & \overset{*}{x}_{n_i+n_{\text{du,bc}}-n_{\text{bc}},1} \\ \vdots & & \vdots \\ \overset{*}{x}_{1,l} & \cdots & \overset{*}{x}_{n_i+n_{\text{du,bc}}-n_{\text{bc}},l} \end{bmatrix} \quad (l \text{ rows, } n_i + n_{\text{du,bc}} - n_{\text{bc}} \text{ columns}) \tag{B.18}$$

B.2.7 Construction of H

An additional matrix $\boldsymbol{H}$ is defined as given in Equation (B.19):

$$\boldsymbol{H} = \begin{bmatrix} 2(\boldsymbol{\Sigma})^{-1}\boldsymbol{Y}^{T} \\ \boldsymbol{D} \end{bmatrix} \tag{B.19}$$

Matrix $\boldsymbol{H}$ has l columns. The number of rows is as follows:

- $2n_{\text{du,bc}} - n_{\text{bc}}$ (for bridging);
- $n_i + 1$ (for normalization);
- $n_i + 2n_{\text{du,bc}} - 2n_{\text{bc}} + 1$ (for bridging and normalization).

B.2.8 Construction of Z

The matrix $\boldsymbol{Z}$ contains the solution (bridged, normalized, or bridged and normalized mole fractions) and can be calculated from Equation (B.20):

$$\boldsymbol{AZ} - \boldsymbol{H} = 0 \tag{B.20}$$

Solving Equation (B.20) to $\boldsymbol{Z}$ gives Equation (B.21):

$$\boldsymbol{Z} = \boldsymbol{A}^{-1}\boldsymbol{H} \tag{B.21}$$

Matrix $\boldsymbol{Z}$ is thus defined as given in Equations (B.22) to (B.24):

$$\boldsymbol{Z}_{\text{br}} = \begin{bmatrix} \overset{*}{x}_{1,1} & \cdots & \overset{*}{x}_{n_{\text{du,bc}},1} \\ \vdots & & \vdots \\ \overset{*}{x}_{1,l} & \cdots & \overset{*}{x}_{n_{\text{du,bc}},l} \end{bmatrix} \quad (2n_{\text{du,bc}} - n_{\text{bc}} \text{ rows, } l \text{ columns}) \tag{B.22}$$

$$\boldsymbol{Z}_{\text{norm}} = \begin{bmatrix} x_{1,1} & \cdots & x_{n_i,1} \\ \vdots & & \vdots \\ x_{1,l} & \cdots & x_{n_i,l} \end{bmatrix} \quad (n_i + 1 \text{ rows, } l \text{ columns}) \tag{B.23}$$

$$\boldsymbol{Z}_{\text{br\&norm}} = \begin{bmatrix} x_{1,1} & \cdots & x_{n_i+n_{\text{du,bc}}-n_{\text{bc}},1} \\ \vdots & & \vdots \\ x_{1,l} & \cdots & x_{n_i+n_{\text{du,bc}}-n_{\text{bc}},l} \end{bmatrix} \quad (n_i + 2n_{\text{du,bc}} - 2n_{\text{bc}} + 1 \text{ rows, } l \text{ columns}) \tag{B.24}$$

B.3 Uncertainty calculation

Solving Equation (B.21) ($\boldsymbol{Z} = \boldsymbol{A}^{-1}\boldsymbol{H}$) requires the calculation of $\boldsymbol{A}^{-1}$ and results in $\boldsymbol{Z}$. The rows of matrix $\boldsymbol{Z}$ contain the bridged, normalized, or bridged and normalized mole fractions. The first x elements on the diagonal of $\boldsymbol{A}^{-1}$ are the uncertainties of these mole fractions where x is equal to:

— $n_{\text{du,bc}}$ (for bridging);

— n_i (for normalization);

— $n_i + n_{\text{du,bc}} - n_{\text{bc}}$ (for bridging and normalization).

Annex C
(informative)

Methane-by-difference approach

C.1 General considerations

While normalization is the state-of-the-art approach to processing raw mole fractions, the methane-by-difference (or “completion”) approach also exists. In this approach to processing the raw mole fractions, all components of the gas are measured apart from methane, which is the major component.

If the methane-by-difference approach is used, calculation of the methane content is achieved by subtracting the sum of the raw mole fractions of all other components from unity. This approach requires either

— the use of pressure correction (see Annex F) to allow the measurement results to be corrected to the same atmospheric conditions at which calibration took place (pressure correction requires the atmospheric pressure to be monitored at the time of injection of each sample), or

— calibration of the analyser immediately prior to, or after, the analysis for each component.

Calibrations may use multi-component mixtures covering all the components and/or binary mixtures (in a methane matrix) for each individual component. The advantage of the latter approach is that the influence of instrumental effect is minimized, meaning that all components are measured independently and are uncorrelated. However, the use of binary mixtures is only advised during stable atmospheric conditions or when pressure correction is used.

C.2 Calculation of processed component mole fractions

In the methane-by-difference approach, all components with the exception of methane are measured. Use of the methane-by-difference approach is applicable when

— analysis is carried out on a component-by-component basis (i.e. not all the components are measured from the same injection into the analysis system), and

— multi-component standards containing the large mole fraction quantities of methane required are not available.

The methane-by-difference mole fractions are calculated using Equations (C.1) and (C.2):

$$x'_i = x^*_i \quad \text{when } i \neq 1 \text{ (methane)} \qquad \text{(C.1)}$$

and

$$x'_1 = 1 - x_{\text{oc}} - \sum_{i=2}^{n_i} x^*_i \quad \text{for methane} \qquad \text{(C.2)}$$

Annex D

(normative)

Relative response factors

D.1 Relative response factors for flame ionization detectors (FIDs)

For an FID, the relative response factors are calculated as the ratio of the carbon number of the reference component to the carbon number of the sample component. Values for FID response factors for reference components propane and *n*-butane[11] are given in Table D.1.

Table D.1 — Relative response factors

Component	Response factor relative to	
	propane	*n*-butane
Propane	1,000	1,333
i-Butane (Methylpropane)	0,750	1,000
n-Butane (Butane)	0,750	1,000
Pentanes	0,600	0,800
Hexanes	0,500	0,667
Heptanes	0,429	0,571
Octanes	0,375	0,500
Benzene	0,500	0,667
Cyclohexane	0,500	0,667
Methylcyclohexane	0,429	0,571
Toluene	0,429	0,571

Response factors other than those listed in Table D.1 may be used, but only with prior justification.

D.2 Relative response factors for thermal conductivity detectors (TCDs)

For a TCD, relative response factors do not follow a simple relationship with component carbon number or relative molar mass, and they can vary between instruments, particularly those with different configurations. For a particular application, they can be determined using appropriate CRMs. If these are not available, they can be determined by analysing a sample gas using an FID, as in D.1, and then again using the TCD. The composition can be calculated from the FID analysis and then used to calculate the TCD relative response factors. Some experimental data are given in Table D.2.

Table D.2 — Experimental response factor data

Component	Response factor (relative to propane)
neo-Pentane (2,2-Dimethylpropane)	0,75
i-Pentane (2-Methylbutane)	0,73
n-Pentane (Pentane)	0,73
n-Hexane (Hexane)	0,64

Response factors other than those listed in Table D.2 may be used, but only with prior justification.

Annex E
(informative)

Testing for outliers

In any set of data, individual results can be found that are not consistent with the other members of that set. These are regarded as outliers or stragglers, and, under the correct circumstances, are eliminated from the data set.

The data is first inspected to identify problems such as transcription errors. The order in which tests are carried out is also relevant, since rogue results can arise in cases where the previous test gas has not been fully purged from the system before the first results from a new test gas are recorded.

Statistical tests (e.g. Grubbs' tests; see the Note below for further information) are then be applied. It is intended that these be used with care and with full understanding of the context within which the measurements were made. Removal of an apparent outlier from a set can result in a revised standard deviation for that set which is obviously much smaller than those of neighbouring sets produced using similar gases during the same test period. In such a case, the apparent outlier is visible within the set, but the set containing it is not inconsistent with its neighbouring sets. An experienced user with detailed knowledge of the application may deem it sensible to ignore the statistical result, and leave the value in.

A difficulty encountered when testing for outliers is that an outlier test that works well with a set containing one rogue result can fail if two or more are present. Furthermore, for two outliers, the test needs to be applied differently when one outlier is low and one high compared to when either both outliers are low or both outliers are high. Careful inspection of the data and knowledge of how the data sets have been derived is therefore very important.

NOTE More detailed information on statistical outlier tests can be found in ISO 5725-1[12], ISO 5725-2[13] and ISO 5479[14].

Annex F
(normative)

Pressure correction during calibration and sample analysis

F.1 General considerations

In natural gas analysis, it is common to equilibrate the sample-loop pressure to the atmospheric pressure prior to injecting the contents of the sample loop into the column(s). This is usually achieved by stopping the sample or calibration gas flow through the sample loop shortly before injection. As the volume and temperature of the sample loop can be assumed to be constant, the amount of substance present in the sample loop is dependent on the sample loop pressure. The detectors used for natural gas analyses (TCDs and FIDs) are, however, independent of atmospheric pressure.

The correction of the detector signal, obtained at a sample loop pressure during injection (p_{inj}), to a reference pressure (p_{ref}) is simply the quotient of both pressures, i.e. $p_{\text{inj}}/p_{\text{ref}}$. For convenience, p_{ref} is often chosen to be 101,325 kPa.

If the sample or calibration gas flow is not stopped before injection, then the pressure at injection will be slightly higher than atmospheric, and so the correction will be an approximation, ignoring the excess pressure above atmospheric. In this case, flows should be kept constant so that the excess pressure remains constant.

F.2 Normalization

The procedure described above is straightforward in gas chromatography for gas analysis. The numerical result of this procedure is, in many cases, very similar to the normalization procedure: correction of the individual mole fractions such that the sum of the mole fractions equals unity. Since there are other, usually smaller, effects that alter sample size, it is still necessary to carry out normalization after pressure correction.

F.3 Calibration

During calibration, the relationship between response and mole fraction is determined by analysing CRMs. For a correct calibration and the calculation of coefficients, it is necessary that the analytical responses at different mole fraction levels be comparable with each other. Because a calibration procedure can take more than several minutes and, in the case of multi-level calibration with multiple reference gas analyses, sometimes several hours, the atmospheric pressure may vary significantly. It is therefore very important that a pressure correction be applied.

For each set of raw data, the atmospheric pressure at time of injection, p_{inj}, is measured. All raw responses are then adjusted to standard pressure by multiplying by $p_{\text{ref}}/p_{\text{inj}}$.

F.4 Sample analysis

Pressure measurement can also recognize and adjust differences in sample (i.e. atmospheric) pressure between sample analysis and calibration, again by multiplying either the response or the calculated quantity by $p_{\text{ref}}/p_{\text{inj}}$. This will result in a sum of raw mole fractions that is much closer to unity that the sum before pressure correction. However, normalization is still required where the normalized mole fraction, x_i, is derived from the raw mole fraction, x^*_i, in accordance with Equation (F.1):

$$x_i = \frac{\dfrac{x_i^* \times p_{\text{ref}}}{p_{\text{inj}}}}{\sum \dfrac{x_i^* \times p_{\text{ref}}}{p_{\text{inj}}}} \tag{F.1}$$

The reference pressure, p_{inj}, is therefore eliminated from the equation.

F.5 Procedure for uncertainty of pressure correction

This clause applies only if this part of ISO 6974 is used in order to calculate uncertainties of component mole fractions in accordance with ISO 6974-2.

If the injection of the contents of the sample loop into the column is carried out at atmospheric pressure and the required calibration period means that pressure variations are likely, the atmospheric pressure shall be measured. This measurement is not free from error, so it is important that its uncertainty be accounted for correctly. (The selected reference pressure has no uncertainty contribution.)

Annex G
(informative)

Software suitable for generalized least squares regression analysis

G.1 General considerations

The three software programs described below are suitable for carrying out the generalized least squares (GLS) analysis described in this part of ISO 6974 and in ISO 6143. Other software packages are commercially available and can be used to carry out GLS analysis, but they will need to be validated by the user.

G.2 XLGENLINE

XLGENLINE is an MS-Excel-based program originally developed for use at the UK National Physical Laboratory (NPL). The program performs a GLS (or OLS) fitting routine and automatically outputs the “unknown” value(s), associated uncertainty, fitted data, goodness-of-fit value and residual deviations. A graphical representation of the fit and the residual deviations is also produced.

The program was validated as follows:

- testing a large set of both artificial and real data sets;
- comparison with B_LEAST (see G.3) and the previous Matlab version of the program (“XGENLINE”);
- testing by technical, mathematical and computing experts at NPL.

Copies of XLGENLINE are available for free download from the NPL website (www.npl.co.uk/content/conForm/28).

G.3 B_LEAST

B_LEAST is an MS-DOS-based program originally developed for use with ISO 6143 by Germany’s Federal Institute for Materials Research and Testing (BAM). The program (written in Power BASIC and compiled into an executable file) performs a GLS fit routine and outputs similar data to XGENLINE. It also allows the fitted function to be plotted in graphical form.

The program was validated as follows:

- testing a large set of both artificial and real data sets;
- comparing with results of Monte Carlo simulations;
- comparing results to those of similar calculations reported in scientific publications;
- testing by experts of ISO Technical Committee ISO/TC 158, *Analysis of gases*.

Copies of B_LEAST are available through DIN (Deutsches Institut für Normung), the German standardization body.

G.4 GasTools

GasTools is an Add-In for MS-Excel (written in VBA). It has a range of numerical calculations — including GLS and OLS fitting, and Monte Carlo simulation.

The program was validated by:

- testing a set of both artificial and real data sets;

- comparing results to those of similar calculations reported in scientific publications;
- comparing results to those from XLGENLINE and B_LEAST;
- testing by experts of ISO Technical Committee ISO/TC 193, *Natural gas*.

Copies of GasTools are available from GL Industrial Services UK Ltd (contact gasvle@gl-group.com).

G.5 Disclaimer

Although provision of the above programs (and associated test files) is made in good faith, there is no implied warranty for their use in contractual or other commercial application, and no guarantee that they are all error-free. However, they have undergone testing and contain no known errors at the time of publication.

Annex H
(informative)

Use of control charts

Control charts can be used to determine whether a chromatographic system is working satisfactorily. Suitable system parameters to monitor are the component retention times (RT) and relative response factors (RRF). The procedure consists of periodically, e.g. daily, injecting a constant composition gas mixture and carrying out a number (n) of consecutive injections — typically five. The mean and standard deviation of the parameters are recorded and compared to the control chart quality lines. The chart shows time versus parameter value and contains five lines: the average (target value), the upper and lower warning lines, and the upper and lower action lines. If the parameters are between the warning lines, then the system is working satisfactorily (although if the parameters are persistently to one side of the average line this may merit further investigation). Between the warning lines and the action lines, no action is taken initially — only if the system does not return to satisfactory behaviour. Outside the action lines, action is taken as soon as possible to correct the system.

In order to create the control chart (known as a Shewhart chart[15]), it is necessary to collect system data for a period during which the system is considered to be operating satisfactorily, e.g. daily for one month. Thus, data for ω periods with n_l injections are collected. The parameters (RT or RRF) of all components are recorded for injection l for period ε, $P_{l,\varepsilon}$. ($l = 1 \ldots n_l$, $\varepsilon = 1 \ldots \omega$). The mean and standard deviation for each period are calculated as given in Equations (H.1) and (H.2):

$$\mu_\varepsilon = \frac{1}{n_l}\sum_{l=1}^{l=n_l} P_{l,\varepsilon} \tag{H.1}$$

$$s_\varepsilon^2 = \frac{1}{\left(n_l - 1\right)}\sum_{l=1}^{l=n_l}\left(P_{l,\varepsilon} - \mu_\varepsilon\right)^2 \tag{H.2}$$

The means and standard deviations of these values over the periods are used to establish the target value and control lines as given in Equations (H.3) and (H.4):

$$\mu_\text{o} = \frac{1}{\omega}\sum_{\varepsilon=1}^{\varepsilon=\omega}\mu_\varepsilon \tag{H.3}$$

$$s_\mu^2 = \frac{1}{\left(\omega - 1\right)}\sum_{\varepsilon=1}^{\varepsilon=\omega}\left(\mu_\varepsilon - \mu_\text{o}\right)^2 \tag{H.4}$$

Typically, warning lines are at $\mu_\text{o} \pm 2s_\mu$ and action lines at $\mu_\text{o} \pm 3s_\mu$.

In practice, chromatographic systems can demonstrate excellent repeatability which results in a very narrow zone between action lines, so wider limits than given above can be more appropriate. These limits would need to be established over a longer period of time.

Bibliography

[1] VARGHA, G., MILTON, M., COX, M. and KAMVISSIS, S., Harmonisation of Coupled Calibration Curves to Reduce Correlated Effects in the Analysis of Natural gas by Gas Chromatography, *J. Chromatogr. A.*, 2005, 1062, pp. 239-245

[2] Recommendation INC-1 (1980), *Expression of experimental uncertainties*

[3] ISO Guide 35, *Reference materials — General and statistical principles for certification*

[4] ISO Guide 34, *General requirements for the competence of reference material producers*

[5] ISO Guide 31, *Reference materials — Contents of certificates and labels*

[6] ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

[7] ISO 10715, *Natural gas — Sampling guidelines*

[8] ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

[9] ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

[10] DRAPER, N.R. and SMITH, H., *Applied Regression Analysis*, 3rd edition, Wiley, New York, 1998

[11] KAISER, R., *Gas Phase Chromatography, Part 3*, Butterworths, London, 1963

[12] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[13] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[14] ISO 5479, *Statistical interpretation of data — Tests for departure from the normal distribution*

[15] ISO 8258, *Shewhart control charts*

[16] ISO 6974-2:2012, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

[17] ISO 6974-3, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 3: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and hydrocarbons up to* C_8 *using two packed columns*

[18] ISO 6974-4, *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+} *hydrocarbons for a laboratory and on-line measuring system using two columns*

[19] ISO 6974-5, *Natural gas — Determination of composition with defined uncertainty by gas chromatography — 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*

[20] ISO 6974-6, *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*

(*Continued from second cover*)

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 6974-5 : 2000 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 5: Determination of nitrogen, carbon dioxide and C_l to C_5 and C_{6+} hydrocarbons for a laboratory and on-line application using three columns	IS 15130 (Part 5) : 2002 Natural gas — Determination of composition with defined uncertainty by gas chromatography: Part 5 Determination of nitrogen, carbon dioxide and C_l to C_5 and C_{6+} hydrocarbons for a laboratory and on-line application using three columns	Identical

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

International Standard	*Title*
ISO 6975 : 1997	Natural gas — Extended analysis — Gas chromatographic method
ISO 10715 : 1997	Natural gas — Sampling guidelines

For tropical countries like India, the standard temperature and the relative humidity shall be taken as 27 ± 2°C and 65 ± 5 percent respectively.

In reporting the results 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 : 1960 'Rules for rounding off numerical values (*revised*)'.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 1986 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Copyright

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 latest issue of 'BIS Catalogue' and 'Standards: Monthly Additions'.

This Indian Standard has been developed from Doc No.: PCD 01 (2888).

Amendments Issued Since Publication

Amendment No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones: 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.gov.in

Regional Offices:		*Telephones*
Central	: Manak Bhavan, 9 Bahadur Shah Zafar Marg NEW DELHI 110002	2323 7617 2323 3841
Eastern	: 1/14, C.I.T. Scheme VII M, V.I.P. Road, Kankurgachi KOLKATA 700054	2337 8499, 2337 8561 2337 8626, 2337 9120
Northern	: Plot No. 4-A, Sector 27-B, Madhya Marg, CHANDIGARH 160019	26 50206 265 0290
Southern	: C.I.T. Campus, IV Cross Road, CHENNAI 600113	2254 1216, 2254 1442 2254 2519, 2254 2315
Western	: Manakalaya, E9 MIDC, Marol, Andheri (East) MUMBAI 400093	2832 9295, 2832 7858 2832 7891, 2832 7892

Branches: AHMEDABAD. BENGALURU. BHOPAL. BHUBANESWAR. COIMBATORE. DEHRADUN. DURGAPUR. FARIDABAD. GHAZIABAD. GUWAHATI. HYDERABAD. JAIPUR. JAMMU. JAMSHEDPUR. KOCHI. LUCKNOW. NAGPUR. PARWANOO. PATNA. PUNE. RAIPUR. RAJKOT. VISAKHAPATNAM.

Published by BIS, New Delhi