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Natural gas — Performance evaluation for analytical systems

Gaz naturel — Évaluation des performances des systèmes d'analyse

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10723 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition cancels and replaces the first edition (ISO 10723:1995), which has been technically revised. It also incorporates Technical Corrigendum ISO 10723:1995/Cor.1:1998.

Introduction

This International Standard describes a method for evaluating the performance of analytical systems intended for the analysis of natural gas. Natural gas is assumed to consist predominantly of methane, with other saturated hydrocarbons and non-combustible gases.

Performance evaluation makes no assumption about equipment for and/or methodology of analysis but gives test methods which can be applied to the chosen analytical system, including the method, equipment and sample handling.

This International Standard contains an informative annex (Annex A) that shows the application for an on-line gas chromatographic system which, as described, is assumed to have a response/concentration relationship for all components that is represented by a straight line through the origin. This International Standard contains an additional informative annex (Annex B) that gives a rationale for the approach used for instrument benchmarking.

Natural gas — Performance evaluation for analytical systems

1 Scope

1.1 This International Standard specifies a method of determining whether an analytical system for natural gas analysis is fit for purpose. It can be used either

a) to determine a range of gas compositions to which the method can be applied, using a specified calibration gas, while satisfying previously defined criteria for the maximum errors and uncertainties on the composition or property or both, or

b) to evaluate the range of errors and uncertainties on the composition or property (calculable from composition) or both when analysing gases within a defined range of composition, using a specified calibration gas.

1.2 It is assumed that

a) for evaluations of the first type above, the analytical requirement has been clearly and unambiguously defined, in terms of the range of acceptable uncertainty on the composition, and, where appropriate, the uncertainty in physical properties calculated from these measurements,

b) for applications of the second type above, the analytical requirement has been clearly and unambiguously defined, in terms of the range of composition to be measured and, where appropriate, the range of properties which may be calculated from these measurements,

c) the analytical and calibration procedures have been fully described, and

d) the analytical system is intended to be applied to gases having compositions which vary over ranges normally found in gas transmission and distribution systems.

1.3 If the performance evaluation shows the system to be unsatisfactory in terms of the uncertainty on the component amount fraction or property, or shows limitations in the ranges of composition or property values measurable within the required uncertainty, then it is intended that the operating parameters, including

a) the analytical requirement,

b) the analytical procedure,

c) the choice of equipment,

d) the choice of calibration gas mixture, and

e) the calculation procedure,

be reviewed to assess where improvements can be obtained. Of these parameters, the choice of the calibration gas composition is likely to have the most significant influence.

1.4 This International Standard is applicable to analytical systems which measure individual component amount fractions. For an application such as calorific value determination, the method will be typically gas chromatography, set up, as a minimum, for the measurement of nitrogen, carbon dioxide, individual hydrocarbons from C_1 to C_5 and a composite measurement representing all higher hydrocarbons of carbon number 6 and above. This allows for the calculation of calorific value and similar properties with acceptable accuracy. In addition, components such as H_2S can be measured individually by specific measurement methods to which this evaluation approach can also be applied.

1.5   Performance evaluation of an analytical system is intended to be performed following initial installation to ensure that errors associated with assumed response functions are fit for purpose. Thereafter, periodic performance evaluation is recommended, or whenever any critical component of the analytical system is adjusted or replaced. The appropriate interval between periodic performance evaluations will depend upon both how instrument responses vary with time and also how large an error may be tolerated. This first consideration is dependent upon instrument/operation; the second is dependent on the application. It is not appropriate, therefore, for this International Standard to offer specific recommendations on intervals between performance evaluations.

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 98-3:2008, *Uncertainty of measurement —Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO 6143:2001, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

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

ISO 6976:1995, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition*

3   Terms and definitions

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

3.1
uncertainty of measurement
parameter, associated with the result of a measurement, that characterizes the dispersion of values that can reasonably be attributed to the measurand

NOTE   In keeping with ISO/IEC Guide 98-3, in this International Standard the uncertainty of the composition is expressed as a standard uncertainty or as an expanded uncertainty calculated through the use of an appropriate coverage factor.

3.2
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   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 3   ISO Guide 31[5] gives guidance on the contents of certificates.

3.3
working measurement standard
WMS
standard that is used routinely to calibrate or verify measuring instruments or measuring systems

[ISO/IEC Guide 99:2007, 5.7]

NOTE   A working measurement standard is usually calibrated against a CRM.

3.4
calibration gas mixture
CGM
gas mixture whose composition is sufficiently well established and stable to be used as a working measurement standard of composition

NOTE   In this International Standard, a CGM is used for routine (e.g. daily) component calibration of the analyser. It is independent of the WMSs used to perform the evaluation.

3.5
response
output signal of the measuring system for each specified component

NOTE   In the case of gas chromatography this will be either peak area or peak height, depending upon the instrument configuration.

3.6
response function
functional relationship between instrumental response and component content

NOTE 1   The response function can be expressed in two different ways as a calibration function or an analysis function, depending on the choice of the dependent and the independent variable.

NOTE 2   The response function is conceptual and cannot be determined exactly. It is determined approximately through calibration.

3.7
calibration function
relationship describing instrument response as a function of component content

3.8
analysis function
relationship describing component content as a function of instrument response

4   Symbols

a_z parameters of the calibration function (z = 0, 1, 2 or 3)

b_z parameters of the analysis function (z = 0, 1, 2 or 3)

x amount fraction of the specified component

$\hat{x}$ adjusted (estimated) amount fraction from the response function

y' raw instrumental response

y corrected instrumental response

s standard deviation of response

$\hat{y}$ adjusted (estimated) response from the response function

F	calibration function
G	analysis function
M	(sample of) reference gas mixture
P	general characteristic (physical property)
p	pressure (in kPa)
u	standard uncertainty
U	expanded uncertainty
k	coverage factor
Γ	goodness-of-fit measure in generalized least squares
δ	error in the estimated value

5 Principle

Performance characteristics of the instrument are determined when used in combination with a specified calibration gas mixture. Therefore, the evaluation procedure can be used to

— determine errors and uncertainties in measured composition and properties over a pre-defined range for each specified component, and

— determine a range for each specified component over which the errors and uncertainties in measured composition and properties do not exceed a predefined measurement requirement.

In each case, the performance characteristics are calculated for the instrument when used in combination with a specified calibration gas mixture of known composition and uncertainty.

NOTE 1   The method can also be used to establish the most appropriate composition of the calibration gas mixture to be used routinely with the instrument such that the errors and uncertainties are minimized over a predefined range of use.

A complete assessment of the errors and uncertainties arising from the use of an instrument could be performed by measuring an infinite series of well-defined reference gas mixtures whose compositions lie within the specified range of operation. However, this is practically impossible. Instead, the principle used in this International Standard is to measure a smaller number of well-defined reference gases and to determine a mathematical description of the response functions for each specified component over a predefined content range. The performance of the instrument can then be modelled offline using these "*true*" response functions, the response functions *assumed* by the instrument's data system and the reference data for the calibration gas mixture specified for the instrument. The measurement of a large number of gas mixtures can then be simulated offline using numerical methods to determine performance benchmarks inherent in the measurement system.

The general procedure for determining the performance characteristics of the instrument is summarized below.

a) Specify the components required to be measured by the instrument and the range for each over which the instrument shall be evaluated.

b) Establish the functional descriptions of the response functions assumed by the instrument (or the instrument's data system) for each specified component.

NOTE 2   These functions are referred to as the *assumed* response functions of the system at the time of calibration/evaluation. These are generally analysis functions used by the instrument to determine the amount from the measured response, $x = G_{asm}(y)$.

c) Establish the composition and uncertainty of the calibration gas mixture specified for routine calibration of the instrument.

d) Design a set of reference gas mixtures with compositions covering all ranges for all components specified in a).

e) Perform a multi-point calibration experiment by collecting instrument response data to measurements of the reference gas mixtures designed and produced in accordance with d). The entire experiment should be conducted within a time period equivalent to that between routine calibrations.

f) Calculate the calibration functions and analysis functions for each specified component using regression analysis and validate the compatibility of the functions with the calibration data set.

NOTE 3   These functions are referred to as the *true* response functions of the system at the time of calibration/evaluation, $y = F_{true}(x)$ and $x = G_{true}(y)$.

g) Calculate instrumental errors and uncertainties for each component and property over a specified range of compositions using the functions and reference data collated in d), e) and f) above.

h) From the distribution of errors and the unbiased uncertainty estimates calculated in g) above, determine the mean error and its uncertainty for each measurand.

The mean errors and their uncertainties on component content and properties resulting from step h) can be compared to performance requirements for the analytical system. If performance benchmarks are poorer than the analytical requirements of the measurement, then it is clear that the method fails to provide the desired performance over the fully specified range. The method shall be modified accordingly and the entire evaluation procedure repeated. Alternatively, the offline calculations shall be repeated over a restricted range of operation in order to improve system performance. In this case, the instrument may be shown to perform adequately over a limited range.

It may be possible to modify the data system on the instrument to allow for the difference between the true response functions and the analysis function assumed by the instrument. In this case, the instrument should be adjusted following the evaluation to account for this difference. If the function form of G_{true} and G_{asm} are the same, then the parameters of G_{asm} in the instrument's data system can be updated with those determined for G_{true} in step f) above, thereby eliminating systematic errors due to the instrument. However, it is important to remember that the parameters of G_{true} are only valid for each component over the content range used to establish the analysis function. That is, the instrument should not be used outside the ranges defined, designed and evaluated in steps a), b) and c).

6 General procedure

6.1 Analytical requirements

6.1.1 General considerations

Users of this International Standard should first decide which components measured by the instrument are to be used in the evaluation of the performance. These are termed *specified components*. For each specified component, the range of amount fractions over which the response function is to be evaluated shall then be decided.

6.1.2 Specified components

For measurement systems set up to determine the major components in natural gas, the components typically specified are nitrogen, carbon dioxide, methane, ethane, propane, 2-methylpropane (*iso*-butane), *n*-butane, 2-methylbutane (*iso*-pentane) and *n*-pentane. In addition, some analytical requirements include 2,2-dimethylpropane (*neo*-pentane). This component is typically present in very low amounts in natural gas and might not be specified in many systems for measurement. In a typical chromatography method, higher hydrocarbons are often specified as a summed component such as hexanes+ (C_{6+}) where

all hydrocarbons containing six carbon atoms or greater are included in one specified component. The instrumental method may measure such a component as an individual chromatographic peak which is typically backflushed through the system, and all components elute at the same time through the detector. Alternatively, in systems where valve switching is not possible, the heavier hydrocarbons elute in a forward fashion through the columns and the component is simply measured as the sum of individual peaks. However, the system may be set up to measure all hexanes (C_6s) individually and the summed peak C_7+ may be specified. This is often the case should the C_6+ amount be significant and a more detailed breakdown of this component be required to minimize errors on the measurement. This principle can be extended such that the system is set up to measure in a C_{6+}, C_{7+}, C_{8+}, C_{9+} or even C_{10+} mode. Users of this International Standard shall decide which of these components are to be included in the evaluation of the instrument's performance based upon the significance of the amounts of each of the components specified in the instrument set-up.

6.1.3 Component content ranges

Once it is clear which measured components are going to be included in the evaluation, the user shall determine, for each of these, over what range of amount fractions the instrument is expected to be used. Such ranges shall generally be greater than that which is expected to be measured by the instrument in regular duty. If the data from the performance evaluation is used subsequently to update the response functions assumed by the instrument, then it is vital that the component content ranges used in the evaluation extend beyond the specified operating range. Should this not be the case, considerable measurement errors might result from extrapolation outside the determined response function.

6.2 Response function types

6.2.1 Assumed functional descriptions

The instrument data system will assume a relationship between response and content of a component in the gas. This is the assumed analysis function of the instrument, $x = G_{asm}(y)$. Many instruments assume a simple first-order polynomial function in the form $x = b_1y$, where b_1 is often referred to as the response factor (RF) for that component. In this case a single calibration gas mixture is used and a first-order response function is assumed, passing through the origin. Alternatively, the instrument may assume a higher-order polynomial functional description or even an exponential or power function.

In some cases the response, particularly for a minor component, may be calculated as relative to that of another (reference) component. Such a relative response factor shall have a response function similar to that of the reference component.

The assumed analysis function for each component, $x = G_{asm}(y)$, shall be noted and used for subsequent calculation of the instrument's performance characteristics described in 6.6.

The function types considered for the treatment of the performance evaluation data shall be matched to those used by the instrument's data system.

NOTE   Occasionally, functional types other than polynomials, such as exponential relationships, are implemented by an instrument's data system. If the instrument uses functional types other than polynomials, it is appropriate to use these in the determination of the analysis functions. However, for the purposes of this International Standard, only polynomial functions up to third order are considered.

6.2.2 Selection of function types

The type of function to be used in practice is chosen according to the response characteristics of the measuring system and that assumed by the instrument's data system.

Polynomial functions describing the true response/amount fraction relationship can be derived in either domain. A mathematical description of instrument response as a function of amount fraction is termed the *calibration function*, whereas that describing amount fraction as a function of response is termed the *analysis function*.

Hence, the true calibration functions, $F_{i,\text{true}}(x_i)$, determined for each component are in the form

$$y_i = F_{i,\text{true}}(x_i) = a_0 + a_1 x_i + a_2 x_i^2 + a_3 x_i^3 \tag{1}$$

where a_z are the parameters of the calibration function.

Similarly, the true analysis functions, $G_{i,\text{true}}(y_i)$, are in the form

$$x_i = G_{i,\text{true}}(y_i) = b_0 + b_1 y_i + b_2 y_i^2 + b_3 y_i^3 \tag{2}$$

where b_z are the parameters of the analysis function.

In both cases

y_i is the mean response of the instrument to component i;

x_i is the amount fraction of component i.

The response functions above are shown in a form up to third order. However, simpler forms up to second order or simply first order may be considered. Choose the form of the response functions with the following considerations:

a)   the simplest form that gives an adequate fit to the data should be used to avoid over-parameterizing the response function;

b)   the number of calibration points, and hence the number of reference gases required to satisfactorily describe a polynomial, increases with the order of the function (see 6.4.2);

c)   if there is an *a priori* reason to assume that a lower-order polynomial will always be suitable, then this should be chosen and a lower number of reference gases may be used (see 6.4.2).

6.3   Calibration gas reference data

6.3.1   General considerations

The performance benchmarks from this evaluation procedure are calculated for the instrument used in combination with the proposed/current calibration gas mixture. This is the working calibration gas used for routine, often daily, calibration.

NOTE   The design of the calibration gas mixture can have significant influence on the distribution of bias errors for the instrument. Similarly, the uncertainties on the amount fraction of each component in the calibration gas can make a significant contribution to the uncertainty on the measurement results. Hence, the design and uncertainty of composition of the calibration mixture shall be chosen carefully.

6.3.2   Composition and uncertainty

The amount fraction, $x_{i,\text{cal}}$, and standard uncertainty, $u(x_{i,\text{cal}})$, for each component in the calibration gas mixture shall be obtained or derived from the certificate of calibration.

If the uncertainty quoted on the certificate is not a standard uncertainty (k = 1), then the standard uncertainties shall be derived using the manufacturer's stated coverage factor.

$$u(x_{i,\text{cal}}) = U_{\text{cert}}(x_{i,\text{cal}}) / k \tag{3}$$

6.4   Working measurement standards (WMS)

6.4.1   Definition

The WMSs used for the determination of the response functions are gas mixtures whose composition is known with a well-defined uncertainty. They may be multi-component or binary mixtures. In all cases, the matrix gas should be methane, so that the behaviour of the WMS is as similar as possible to that of natural gases. Binary mixtures can generally be prepared with lower uncertainties than multi-component mixtures. However, many more mixtures shall be made; one set for each non-methane component to be tested. Generally, multi-component mixtures should be used as they allow more repeat measurements to be performed for each component/amount fraction combination.

The WMS should be chosen so as to be suitable for the intended analytical application as discussed in 6.1. However, it is not practicable to manufacture and calibrate WMSs which contain all the components in natural gas, given the complexity of the higher hydrocarbons that are commonly found and the difficulty of preparing high-quality mixtures containing condensable components. In the majority of applications, the major components in natural gas, nitrogen, carbon dioxide, methane, ethane, propane, 2-methylpropane (*iso*-butane) and *n*-butane are generally specified and normally included in the reference gas mixtures. In addition, 2-methylbutane (*iso*-pentane), *n*-pentane and a representative C_{6+} component such as *n*-hexane are often included. If 2,2-dimethylpropane (*neo*-pentane) is a specified component in the analytical requirement, it may also be included in the WMS. Any component expected to be present in an amount fraction greater than 0,01 should be included.

NOTE   The WMS used in this evaluation procedure can also be used to define the analysis function of an analyser when it is initially installed or on other occasions when a primary calibration is required to define the analysis function assumed by the instrument's data system.

6.4.2   Composition and uncertainties

For each specified component that will be included in the WMS, the number of levels, calibration points, at which the evaluation shall be performed depends upon the form of the function type selected for the evaluation (see 6.2.2).

The minimum number of calibration points recommended to give sufficient degrees of freedom for the unbiased estimate of the response function is as follows:

3 (three)   for a first-order polynomial;

5 (five)   for a second-order polynomial;

7 (seven)   for a third-order polynomial.

The WMSs shall be selected such that their amount fractions are approximately equally spaced across the defined evaluation range (see 6.1.3) with one at (or below) the lower limit and one at (or above) the higher limit.

NOTE 1   Depending on the intended application, the lower end of the range might be close to the limit of detection, in which case it might not be possible to include a component amount fraction below the lower end of the application range.

In the design of the recipe of the set of WMSs, the user shall be careful not to include all high-amount fractions of the higher hydrocarbons together in the same mixture. Should this be the case, the pressure of the mixture would be limited due to the potential of retrograde hydrocarbon condensation due to the high dewpoint of the mixture. The higher amounts of higher hydrocarbons should, where possible, be distributed amongst the set of WMSs.

Once designed and manufactured, the composition and uncertainties of the WMS should be determined by a comparison method in accordance with ISO 6143. Certified reference gas mixtures (CRMs) of an appropriate metrological quality shall be used as the source of traceability for this comparison step. Whether binary or multi-component mixtures are used, each WMS shall have compositional

uncertainties which are small by comparison with the anticipated measurement uncertainties of the analytical system under evaluation.

NOTE 2   Helium, C_5 and heavier hydrocarbons are usually present at sufficiently low mole fractions that nonlinearity of response is unlikely to be a problem. If not specified in the reference gas mixtures, the assumption of a first-order response/amount fraction relationship can be tested using natural gases of certified composition containing these components covering a range of amount fractions appropriate to the application.

6.5   Experimental design

6.5.1   General considerations

Each WMS shall be measured several times by the instrument in order to obtain a reasonable estimate of the response functions for each component. It is strongly recommended that each gas be analysed 10 times. However, where this number of repeats would be impractical (for example requiring the test period to extend beyond the normal calibration interval), a smaller number of repeats may be used, but not less than six. When changing between WMSs, regulators, valves and tubing need to be fully purged otherwise the first or more replicates of a fresh WMS may not be fully representative of the gas contained within the cylinder. The measurement might be biased due to the presence of residues of the preceding gas or of the ingress of air occurring during changeover.

The entire calibration procedure is likely to take several hours depending upon the instrument cycle time. Over such a period, it is quite common for the ambient atmospheric pressure to change by as much as 0,5 % relative and in extreme cases by up to 2 % relative. Gas samples are typically introduced into analysers by being purged through an injector device to a vent which is at, or referenced to, atmospheric pressure. Hence, ambient pressure variations cause a change in the effective sample size. This has the effect of raising or decreasing the response of the instrument to the same gas mixture. Hence, there will be an inherent drift in the absolute response of the instrument over time, dependent upon the change in atmospheric pressure over that period. There are other parameters that influence the effective sample size or the detector sensitivity, but atmospheric pressure variation is the most significant.

There is a choice of procedures for the measurement of each reference gas which depends on the availability of time and equipment. There are two general approaches to implementing the calibration procedure which are termed as follows:

a)   batch-wise calibration;

b)   drift compensation calibration.

The first, in which replicate measurements of each mixture are carried out in sequence, is the most practical implementation but has the disadvantage of not compensating for the inherent drift in a system over the time of the calibration. The second, in which replicate measurements of each mixture are performed separately and independently, will compensate for the inherent instrumental drift over the time of the calibration but is considerably more time-consuming and more suited to implementation in an automated system.

Whichever experimental procedure is used, the entire calibration experiment should be conducted within a time period equivalent to that between routine calibrations.

6.5.2   Batch-wise calibration

The WMSs are introduced in sequence, with all the replicate measurements on the first gas being completed before the second is introduced and so on. The sampling sequence in time is:

$M_{1,1}, M_{1,2}, M_{1,3}, ..., M_{1,n}$ (n replicate measurements in succession on gas M_1), then

$M_{2,1}, M_{2,2}, M_{2,3}, ..., M_{2,n}$ (n replicate measurements in succession on gas M_2), then

$M_{p,1}, M_{p,2}, M_{p,3}, ..., M_{p,n}$ (n replicate measurements in succession on gas M_p).

This is the simplest and most practicable method for a manually implemented field-use application as it requires only the changeover of p gases on the test instrument. However, the change in atmospheric pressure during the test will have a greater influence on the variation between the reference gases than within the repeat measurements for any single one.

Significant instrumental drift between gases will likely give rise to higher residuals and hence poor goodness-of-fit parameters in the generalized least-squares regression procedure. To minimize the goodness-of-fit parameters, it may be necessary to correct for the instrumental drift by correcting for the effective sample size of each reference gas mixture at the time of injection. This can be done by drift correction (6.5.4).

6.5.3   Drift compensation calibration

This procedure separates the repeat measurements on each reference gas mixture in such a way as to limit the effect of sample size variations and compensate for the instrumental drift over the calibration period.

The sampling sequence in time is:

$M_{1,1}, M_{2,1}, M_{3,1}, ..., M_{p,1}$ (1st repeat measurement on each of p gases), then

$M_{1,2}, M_{2,2}, M_{3,2}, ..., M_{p,2}$ (2nd repeat measurement on each of p gases), then

$M_{1,n}, M_{2,n}, M_{3,n}, ..., M_{p,n}$ (nth repeat measurement on each of p gases).

The first repeat measurement on reference gas 1 is followed by the first on gas 2 and so on. Then the second repeat on reference gas 1 follows the completion of the first repeat measurement on all p reference gases. This procedure is continued throughout the number of repeats required.

This approach ensures that variations due to external influences are shared or smeared out throughout the repeats on each reference gas. The instrumental drift is effectively compensated for by the experimental procedure. This occurs in such a way that the within-gas variations may be higher but the between-gas variations are more consistent. With this approach, the goodness-of-fit parameters in the generalized least squares regression procedure are usually good.

The major disadvantage to this method is that the gases have to be changed much more frequently. In addition, after each change, it is advisable for at least one and possibly two analyses to be performed before data are recorded, to allow for sufficient purging between the gases. This means that the procedure is much lengthier than the first, and, to be practicable, requires an automated changeover and purging system to handle the introduction of the reference gases.

6.5.4   Drift correction

During either of the two experimental procedures described above (6.5.2 or 6.5.3), the instrumental response may be corrected for drift due to changes in atmospheric pressure (for reasons described earlier). The atmospheric pressure is measured and recorded at the start of each repeat on each of the WMSs. This allows the pressure-influenced variations in sample size to be corrected to a reference value. In this way the data will be more consistent both within and between reference gases. While this approach may be used for the drift-compensation-type calibration (6.5.3), it is often more useful to correct instrumental responses obtained during batch-wise calibration as the result of this experimental approach is much more sensitive to instrumental drift.

NOTE   If time and automation techniques are available, the combination of a drift compensation experiment with drift correction for atmospheric pressure will lead to the most precise and inter-consistent calibration data set.

6.5.5   Collation of calibration data

Whichever calibration method is used, the collation of raw calibration data are identical. For each of q components, (i = [1, ..., q]), at each of p amount fractions, (j = [1, ..., p]), collect n (preferably 10) repeat measurements, (k = [1, ..., n]). Collate each instrument response, y'_{ijk}, with the corresponding component amount fraction, x_{ij}.

If pressure correction (drift correction) is not used, set y_{ijk} equal to y'_{ijk}. Alternatively, record the atmospheric pressure, P_{ijk}, in kPa, at the start of each instrument cycle, and correct the analyser response data for atmospheric pressure according to

$$y_{ijk} = \frac{P_{\text{ref}}}{P_{ijk}} \times y'_{ijk}$$

(4)

where P_{ref} is a reference pressure in kPa, such as 101,325 kPa.

Group the calibration data by component and level, y_{ij1}, y_{ij2}, y_{ijn}. Inspect each group for outliers or stragglers using Grubbs' test or some other suitable outlier test.

NOTE 1   In any set of data, individual results can be found which are not consistent with the other members of that set. These are regarded as outliers or stragglers, and can be eliminated from the data set according to the recommendations of the outlier test used. Inspection of the data is the first stage, identifying problems such as transcription errors. The order in which tests were carried out is also relevant, since rogue results can arise in cases where the previous test gas was not fully purged from the system before the first results from a new test gas are recorded. More detailed information on statistical outlier tests can be found in ISO 5725-1[7], ISO 5725-2[8] and ISO 5479[9].

After rejection of any outliers, calculate the mean response, y_{ij}, standard deviations, s_{ij}, and adjusted numbers of analyses, n_{ij} for q components, ($i = [1, ..., q]$), and at each of p amount fractions, ($j = [1, ..., p]$). For the purposes of this method, an estimate of the standard uncertainty on the mean response for each component at each level, $u(y_{ij})$, is given simply by the standard deviation of repeat measurements, s_{ij}.

NOTE 2   An estimate of $u(y_{ij})$ using the standard deviation of the mean, where $u(y_{ij}) = s_{ij}/\sqrt{n}$, would most likely underestimate the uncertainty as all measurements were likely not made independently under appropriate reproducibility conditions.

6.6 Calculation procedures

6.6.1 General considerations

The relationship between component amount fraction and instrument response is found by regression analysis, using the technique of generalized least squares (GLS) in accordance with ISO 6143:2001,A.2. This procedure takes account of the uncertainties in both the independent and dependent variables, and allows calculation of overall uncertainty to include contributions from the uncertainties in the reference gas compositions, analyser response and the parameters of the response functions resulting from the regression procedure.

NOTE   The advice in this section applies to use of GLS to determine regression functions. For ordinary least squares (OLS) methods, a statistical test, for example a sequential F-test[14] should be used to determine the appropriate order of the polynomial function.

In practice, the response functions are calculated independently in both domains, yielding the true *calibration function*, $F_{\text{true}}(x_i)$, and the true *analysis function*, $G_{\text{true}}(y_i)$.

The true calibration function is used in combination with the instrument's assumed analysis function, and the working calibration gas composition and uncertainty, to determine performance benchmarks in terms of errors in measured compositions and properties, together with the uncertainties in these errors.

The true analysis function can be used subsequently, post-evaluation, to update the instrument's assumed analysis function. Following such an adjustment, instrumental errors will be minimized.

6.6.2 Regression analysis

For each of q components, ($i = [1, ..., q]$), construct a data set of input parameters for the regression analysis at each of p amount fraction levels, ($j = [1, ..., p]$), giving

$$[x_{ij}, u(x_{ij}), y_{ij}, u(y_{ij})]$$

where

x_{ij} is the amount fraction of component i in reference gas mixture j;

$u(x_{ij})$ is the standard uncertainty on the amount fraction x_{ij};

y_{ij} is the mean response of n_{ij} observations following the removal of any statistical outliers;

$u(y_{ij})$ is an estimate of the standard uncertainty of the mean response y_{ij}.

The parameters of the analysis function, b_z, and of the calibration function, a_z, are then calculated by GLS regression analysis.

6.6.3 Validation of the response functions

Each of the candidate analysis and calibration function types (first-, second- and third-order polynomial functions) are taken in turn and the set of normal equations constructed. These equations are solved in accordance with ISO 6143:2001, A.2, and the parameters b_z and a_z determined for each order.

A satisfactory fit is required for each individual point by using the following test procedure. For each experimental point (x_{ij}, y_{ij}), an adjusted point $(\hat{x}_{ij}, \hat{y}_{ij})$ is calculated, as a by-product of the regression analysis used to determine the response function. The coordinates $\hat{x}_{ij}$ and $\hat{y}_{ij}$ of the adjusted point are estimates of the true analyte content and of the true response, respectively, for the WMS M_{ij} ($j = [1, ..., p]$). 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 point ($j = [1, ..., p]$):

$$\left|\hat{x}_{ij} - x_{ij}\right| \leq ku(x_{ij}) \text{ and } \left|\hat{y}_{ij} - y_{ij}\right| \leq ku(y_{ij}) \tag{5}$$

NOTE   In almost all cases, this condition is equivalent to requiring that the calculated response curve pass through every experimental "calibration rectangle", $[x_{ij} \pm ku(x_{ij}), y_{ij} \pm ku(y_{ij})]$, based on the expanded uncertainty $U = ku$ with a coverage factor of $k = 2$.

To effectively test the compatibility of a prospective analysis or calibration function, calculate the measure of goodness of fit, Γ, defined as a maximum value of the weighted differences $\left|\hat{x}_{ij} - x_{ij}\right| / u(x_{ij})$ and $\left|\hat{y}_{ij} - y_{ij}\right| / u(y_{ij})$, between the coordinates of measured and adjusted calibration points ($j = [1, ..., p]$). A function is admissible if $\Gamma \leq 2$.

If the model validation test fails for a particular order, examine other polynomial response models until a model is found that is compatible with the calibration data set.

If several functions are considered and found to be admissible, make the final choice as follows:

a) If a physical model of the response behaviour of the analytical system is available, and if the function corresponding to this model is admissible, use this function.

b) If no such physical model is available, and if several functions give about the same fit, i.e. similar values of the goodness-of-fit parameter Γ, use the simplest function, i.e. the one with the lowest number of parameters.

c) If no physical model is available and admissible functions differ considerably with respect to their fit, use the function which gives the best fit, with the lowest value of Γ.

In addition to the procedures described above, every calculated response function shall be inspected visually. This visual inspection is necessary to reveal nonsense correlations over the specified range for the component which can occur without being detected by local examination of the curve fit to the calibration points. Such nonsense functions are liable to occur in the case of 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. Then this calibration point is given erroneously a very high weight. Consequently, the response curve is forced through this point with little importance given to the other calibration points.

In some circumstances, the calibration data set can be inconsistent to such an extent that none of the polynomial functions is acceptable as $\Gamma > 2$ for all trial response functions. For example, this can occur frequently following a batch-wise calibration where there has been significant instrument drift during the day and drift correction was not possible.

6.6.4   Errors

6.6.4.1   General considerations

In its calculation of the amount fraction of each component ($i = [1, ..., q]$), the instrument assumes an analysis function, $x_i = G_{i,\mathrm{asm}}(y_i)$, in the inverse domain of the calibration function. The amount fraction reported by the analyser will be in error for any component whose true response deviates from this assumed behaviour. Errors are determined by comparing the composition calculated from the *true* instrument response with that assumed by the data system. In addition, the distribution of errors is significantly dependent upon the calibration gas composition in use with the instrument. Hence, errors should be calculated for the instrument in combination with the composition of the calibration gas mixture currently in use.

6.6.4.2   Content (amount fraction)

The analysis function assumed by the instrument's data system, determined in 6.2.1, can be described as

$$x_i = G_{i,\mathrm{asm}}(y_i) \tag{6}$$

Similarly, the true calibration function, determined by the performance evaluation procedure above is described as

$$y_i = F_{i,\mathrm{true}}(x_i) \tag{7}$$

At the point of calibration these functions are coincident such that the measured amount fraction of component i, $x_{i,\mathrm{meas}}$, is

$$x_{i,\mathrm{meas}}^* = x_{i,\mathrm{cal}} \times \frac{G_{i,\mathrm{asm}}\left[F_{i,\mathrm{true}}(x_{i,\mathrm{true}})\right]}{G_{i,\mathrm{asm}}\left[F_{i,\mathrm{true}}(x_{i,\mathrm{cal}})\right]} \tag{8}$$

Hence, for a *true* amount fraction of $x_{i,\mathrm{true}}$, in the measured gas sample, using a calibration gas of composition $x_{i,\mathrm{cal}}$, the measured non-normalized amount fraction is $x_{i,\mathrm{meas}}^*$.

The absolute error in the measured amount fraction can then be determined following normalization of the resulting composition for all components.

$$x_{i,\,\text{meas}} = \frac{x^*_{i,\,\text{meas}}}{\sum_i x^*_{i,\,\text{meas}}} \tag{9}$$

Hence, the estimated error on the determination of each component, δx_i, is

$$\delta x_{i,\,\text{meas}} = x_{i,\,\text{meas}} - x_{i,\,\text{true}} \tag{10}$$

Errors on the normalized amount fraction shall be determined repeatedly by this offline model using Monte-Carlo methods. A data set of at least 10 000 hypothetical compositions of natural gas shall be constructed where each gas component amount fraction lies within the range of gases possible through the measurement point and defined in 6.1.3.

In order to more accurately model the measurement, the compositions generated and used in the simulation should not be strictly random. The compositions should be derived using a set of known rules relating the amounts of one component to that of the next hydrocarbon in the homologous series. The algorithm used for the generation of the natural gas compositions should also contain rules relating the isomers of butane and pentane to the normal isomer in each case. By this method, *non-naturally occurring* natural gas compositions, which would not be present in a real sample, are not generated during the simulation.

6.6.4.3   Characteristics (physical properties)

During each trial in the simulation above, a set of actual and measured compositions arise consisting of amount fractions $x_{i,\,\text{true}}$ and $x_{i,\,\text{meas}}$ respectively.

Errors in physical properties are obtained by calculating the difference between the property determined from the true composition and that of the measured composition.

For example, the real superior calorific value on a volumetric basis, in MJ·m^{-3}, at specified combustion and metering temperatures and a specified pressure determined using ISO 6976, is given by

$$CV = \tilde{H}_S[t_1, V(t_2, p_2)] = \frac{\tilde{H}^0_S[t_1, V(t_2, p_2)]}{Z_{\text{mix}}(t_2, p_2)} = \frac{\sum\limits_{i=1}^{N} x_i \times \tilde{H}^0_i[t_1] \times \dfrac{p_2}{R \cdot t_2}}{1 - [\sum\limits_{i=1}^{N} x_i \times \sqrt{b_i}]^2} \tag{11}$$

where

t_1 is the combustion temperature in K;

t_2 is the metering temperature in K;

p_2 is the metering pressure in kPa;

$\tilde{H}^0_i[t_1]$ is the ideal superior calorific value on a molar basis (kJ·mol^{-1}) at combustion temperature t_1 for component i [ISO 6976:1995, Table 3];

R is the molar gas constant (8,314 472 J·mol^{-1}·K^{-1});

b_i is the mole fraction summation factor at the specified temperature and pressure.

Substituting $x_{i,\,\text{true}}$ and $x_{i,\,\text{meas}}$ into the right-hand side of this equation, we obtain CV_{true} and CV_{meas} respectively.

Then

$$\delta CV_{\mathrm{meas}} = CV_{\mathrm{meas}} - CV_{\mathrm{true}} \tag{12}$$

Similar expressions can be derived for the errors in other properties using the same principles.

6.6.4.4 Error distribution

For each of the 10 000 hypothetical natural gas compositions, the errors for each component and on the measured physical properties shall be calculated as above. The resulting distribution of errors is sorted and inspected to give the minimum, mean and maximum errors in each component and on any physical properties chosen to be critical measurands in the process. Such errors are performance benchmarks for the instrument over the range of compositions specified for measurement by the instrument.

6.6.5 Uncertainties in errors

6.6.5.1 General

As there is no uncertainty in the true value of the hypothetical amount fractions and the properties calculated from them, the uncertainties in the errors, $u(\delta x_i)$ and $u(\delta P)$, are equal to the uncertainty in the measured amount fraction, $u(x_{i,\,\mathrm{meas}})$, and the calculated properties, $u(P_{\mathrm{meas}})$, respectively.

6.6.5.2 Content (amount fraction)

Determination of the uncertainties on the unbiased measurement of the amount fraction, $u(x_{i,\,\mathrm{meas}})$, shall be carried out in accordance with the relevant sections of ISO 6974-2.

6.6.5.3 Characteristics (physical properties)

Determination of the uncertainties on the unbiased measurement of physical properties, $u(P)$, calculated from composition shall be derived from $u(x_{i,\,\mathrm{meas}})$ and other sources of uncertainty in accordance with the relevant sections of ISO 6976.

In principle, calculation of other physical properties, determined from composition, can be performed using other methods outside the scope of ISO 6976 provided those properties are calculated by an agreed or approved method and that the uncertainties on these properties are calculated in accordance with ISO/IEC Guide 98-3.

6.6.6 Instrument benchmarking

The preceding sections have described how for each of a given set of N hypothetical compositions the error in the measured amount fraction and any appropriate property calculable from the composition is calculated, together with the uncertainty in the error in amount fraction (or calculated property). This information is converted to a single mean error and uncertainty, as outlined below, so as to benchmark the performance of the instrument when analysing specified gases using a specified working calibration gas. Annex B outlines a justification for the approach adopted which is in accordance with ISO/IEC Guide 98-3.

Compute the mean error in amount fraction and properties, as appropriate, from

$$\overline{\delta P} = \frac{\sum_{t=1}^{t=N} \delta P_t}{N} \tag{13}$$

where δP_t is the error (in either component amount fraction or property) calculated for the tth of N hypothetical compositions.

Compute the standard uncertainty in the mean error determined above from the positive square root of

$$u_c{}^2\left(\overline{\delta P}\right) = \overline{u^2\left[\delta P(t)\right]} + u^2\left(\overline{\delta P}\right) \tag{14}$$

where

$\quad u^2\left(\overline{\delta P}\right) \quad$ is the variance of the errors calculated for each of the N hypothetical compositions, and

$\quad \overline{u^2\left[\delta P(t)\right]} \quad$ is the arithmetic mean of the squared standard uncertainties in error, , calculated for each of the N hypothetical compositions.

Compute the expanded uncertainty in mean error by use of an appropriate coverage factor, k:

$$U_c\left(\overline{\delta P}\right) = k \times u_c\left(\overline{\delta P}\right) \tag{15}$$

7   Interpretation

7.1   General considerations

The performance of the instrument is concisely expressed by the mean error and its expanded uncertainty.

This information may be used in one of two ways:

a)   to compare the performance for the range of hypothetical compositions of interest with a pre-defined performance specification, or

b)   to determine a range for each specified component over which errors in measured composition or properties do not exceed a pre-defined requirement.

7.2   Pre-defined performance specification

Typically, the required performance of the instrument is specified in terms of the maximum permissible error (MPE) and maximum permissible bias (MPB). Compliance with such a specification would be established if:

$$\left|\overline{\delta P}\right| + U_c\left(\overline{\delta P}\right) \le MPE \tag{16}$$

and

$$\left|\overline{\delta P}\right| \le MPB \tag{17}$$

7.3   Determination of the analytical range of the instrument

a)   Carry out the performance evaluation for the initial choice of range in specified components. Assess instrument performance by comparison with the pre-defined MPE and MPB as outlined in 7.2.

b)   If instrument performance is not compliant, reduce the range in one or more components and repeat the calculations using a new set of hypothetical compositions with the restricted range and again compare with the pre-defined MPE and MPB.

c)   Repeat steps a) and b) until a range for each component results in a satisfactory instrument performance.

d)   If instrument performance determined initially in a) is in compliance with the pre-defined requirement, a wider range, in one or more components, may be selected and steps a) and b) repeated until a desired analytical range is obtained.

7.4 Criteria for selection of hypothetical compositions

The value of mean error and its uncertainty calculated in 6.6.6 are dependent upon the choice of hypothetical compositions used during the simulation. When assessing whether evaluation results meet pre-defined instrument performance criteria, it is therefore essential that the following factors be considered:

a) The value of MPE may be chosen based on regulatory or contractual requirements or simply based on user criteria (specified limit). It is often chosen statistically so that the associated probability that an instrument error will exceed the MPE can be predicted (on the basis that MPE reflects a probability level associated with the coverage factor, k) when analysing gases within its specified analytical range. With respect to the choice of compositions for use during simulation, a random selection of hypothetical compositions from the analytical range, in which component amount fractions are uncorrelated, may be acceptable, even though some of the hypothetical compositions are untypical of natural gas.

b) The value of MPB may be chosen based on similar considerations as for MPE. The MPB is selected such that, over an extended period of time, any consistent error in the measured composition and properties are small enough as to be considered acceptable (i.e. the instrument shows no significant bias). In this situation, random selection of hypothetical compositions and uncorrelated amount fractions is not appropriate and the hypothetical compositions should be representative of either the gases actually presented to the instrument (if retrospective compliance with a performance requirement is being assessed) or the gases that are likely to be presented to the instrument in the future (if future compliance with a performance specification is being assessed).

Annex A
(informative)

Example of application using chromatography

A.1 Analytical requirement

An on-line instrument to provide a compositional analysis of natural gas is required, from which the gross calorific value is to be calculated using the method described in ISO 6976. Components to be measured are nitrogen, carbon dioxide, and all saturated hydrocarbons in the range C_1 to C_5. Components of carbon number greater than 5 may be measured individually or as a composite "pseudo-component" referred to as C_{6+}. If these components are measured individually they will be summed after the analysis to give a C_{6+} value. The helium content of the gas to be analysed may be assumed to be zero. The instrument will function principally as a calorific value determination device and the required performance is specified as shown in the following example.

Required performance:

Gross calorific value, calculated for the real gas at reference conditions of 15 °C (combustion) and 15 °C, 1,013 25 bar (metering). For calculation of the gross calorific value, the C_{6+} component is to be assigned the pure component properties of n-hexane.

Maximum permissible error (MPE): 0,1 MJ·m^{-3}

NOTE 1   MPE is applicable to any composition within the specified analytical range of the instrument. Compliance with MPE to be assessed at the 95 % level using a coverage factor of $k = 2$.

Maximum permissible bias (MPB): 0,025 MJ·m^{-3}

NOTE 2   MPB is applicable only to compositions expected during normal operation of the instrument.

Analytical range of the instrument (%mol/mol):

Component	Min.	Max.
nitrogen	0,10	12,00
carbon dioxide	0,05	8,00
methane	64,00	98,50
ethane	0,10	14,00
propane	0,05	8,00
iso-butane	0,010	1,20
n-butane	0,010	1,20
neo-pentane	0,005	0,05
iso-pentane	0,005	0,35
n-pentane	0,005	0,35
n-hexane	0,005	0,35

NOTE 3　The specification given above is illustrative only and is not intended to indicate or imply appropriateness for any application. It is intended that users of this International Standard assess the appropriate performance level for their specific requirements.

NOTE 4　The required performance of this measurement device is specified only in terms of a single physical property calculated from composition. Should a specification define a performance in terms of the measured amount fractions, these can then be determined in accordance with 6.6.5.2.

A.2　Description of method

The analytical method is designed for the measurement of nitrogen, carbon dioxide, methane, ethane, propane, two butanes, three pentanes and total hexanes+ in natural gas. The method is intended for on-line use and does not distinguish oxygen from nitrogen.

The method uses gas chromatography with a thermal-conductivity detector and helium carrier gas. A boiling-point column is used for propane and heavier hydrocarbons. A switching valve diverts the lighter components, nitrogen, carbon dioxide, methane and ethane, onto a porous polymer bead column where they are stored and analysed later in the cycle. The boiling-point column is divided into two sections, with the shorter pre-section used for rapid backflush of hexanes+ to the detector.

Calibration is performed using a single calibration mixture at 24-hour intervals and the data handling assumes that the shape of the response curve for each component is a straight line through the origin (i.e. the assumed response function is $x_i = b_{1,i} y_i$). The composition of the calibration gas, together with the uncertainty in its composition, is given below.

Component	x_i	$U(x_i)$	$u(x_i)$
nitrogen	4,50	0,027 0	0,013 5
carbon dioxide	3,30	0,013 0	0,006 5
methane	80,46	0,090 0	0,045 0
ethane	7,00	0,031 0	0,015 5
propane	3,30	0,011 0	0,005 5
iso-butane	0,50	0,002 8	0,001 4
n-butane	0,50	0,003 2	0,001 6
neo-pentane	0,11	0,001 8	0,000 9
iso-pentane	0,11	0,001 0	0,000 5
n-pentane	0,11	0,001 4	0,000 7
n-hexane	0,11	0,001 8	0,000 9

NOTE　Composition and expanded uncertainty were taken from the certificate of calibration issued by a laboratory accredited to ISO/IEC 17025. Standard uncertainty was calculated from expanded uncertainty using a coverage factor of k = 2, which was taken from the certificate of calibration.

A.3　Working measurement standards

Seven WMSs were prepared containing nitrogen, carbon dioxide, methane, ethane, propane, *iso*-butane, *n*-butane, *neo*-pentane, *iso*-pentane, *n*-pentane and *n*-hexane at amount fractions that span the range described in the analytical requirement. The compositions of these mixtures, labelled 401 to 407, are given in Table A.1. The uncertainties in the composition of these mixtures are given in Table A.2.

A performance evaluation was conducted using the batch-wise experimental design. No correction was made for potential drift in the instrument over the period of the evaluation. Table A.3 gives the area counts of each of six analyses of each of these mixtures, following outlier removal.

A.4 Calculations

A.4.1 Regression analysis

The parameters of the analysis function, b_z, and of the calibration function, a_z, as calculated by GLS regression are given in Table A.4 for polynomials of orders 1, 2 and 3.

A.4.2 Validation and selection of analysis and calibration functions

Inspection of the goodness of fit, Γ, for each trial function in Table A.4 and application of the guidance given in 6.6.3 leads to the choice of analysis and calibration functions given in Tables A.5 and A.6, respectively.

A.4.3 Errors in calorific value and their uncertainties

A data set of 10 000 hypothetical compositions of natural gas is devised using Monte-Carlo methods, where each component lies within the analytical range specified in A.1. A small selection of the hypothetical compositions is given in Table A.7. For each hypothetical composition, the error in mole fraction of each component and any calculated property is determined. The analytical requirement specified in A.1 requires errors in gross calorific values and the uncertainties in errors in gross calorific values to be determined; this is illustrated, using expanded uncertainties, in Table A.8.

A.4.4 Mean error in gross calorific value and its uncertainty

The mean error in gross calorific value is determined from the mean of the errors, i.e.

$$\overline{\delta P} = [(-0{,}039) + (-0{,}089) + \ldots + (0{,}032) + (0{,}053)]/10\ 000 = 0{,}000\ 05 \text{ MJ·m}^{-3} \tag{A.1}$$

The variance in the mean error in gross calorific value is determined from

$$u_c^{\ 2}(\overline{\delta P}) = \overline{u^2\left[\delta P(t)\right]} + u^2(\overline{\delta P}) \tag{A.2}$$

$$= [(0{,}033^2 + 0{,}026^2 + \ldots + 0{,}025^2 + 0{,}031^2)/10\ 000]$$

$$+ [(-0{,}039 - 0{,}000\ 05)^2 + (-0{,}089 - 0{,}000\ 05)^2 + \ldots + (-0{,}032 - 0{,}000\ 05)^2 + (0{,}053 - 0{,}000\ 05)^2]/10\ 000$$

$$= 0{,}000\ 85$$

Hence $u(\delta GCV) = 0{,}029\ 19 \text{ MJ·m}^{-3}$ and $U(\delta GCV) = 0{,}058\ 37 \text{ MJ·m}^{-3}$, assuming a coverage factor of $k = 2$.

A.5 Interpretation of results

A.5.1 Pre-defined performance specification

The required performance is expressed in terms of maximum permissible error and maximum permissible bias.

$$\text{MPE:} \quad \left| \overline{\delta GCV} \right| + U_c\left(\overline{\delta GCV} \right) = 0{,}000\ 05 + 0{,}058\ 37 = 0{,}058\ 42\ \text{MJ·m}^{-3} \tag{A.3}$$

Performance is compliant with the specified MPE of 0,1 MJ·m^{-3}.

$$\text{MPB:} \quad \left| \overline{\delta GCV} \right| = 0{,}000\ 05\ \text{MJ·m}^{-3} \tag{A.4}$$

Performance is compliant with the specified MPB of 0,025 MJ·m^{-3}.

A.5.2 Determination of the analytical range of the instrument

If the instrument is not compliant with the performance specification for the specified analytical range, repeat A.4.3 and A.4.4 using a reduced range in one or more components and compare against the pre-defined MPE and MPB.

Alternatively, if the instrument is compliant, a wider analytical range may be explored by repeating A.4.3 and A.4.4 using an enlarged range in one or more components and comparing with the pre-defined MPE and MPB.

Table A.1 — Composition of the WMSs (% mol/mol)

	401	402	403	404	405	406	407
nitrogen	0,103 3	0,987 6	2,507 8	4,434 6	6,453 6	8,972 2	11,941 2
carbon dioxide	0,047 5	1,490 1	7,955 5	2,981 7	0,501 5	6,034 5	4,500 5
methane	98,459 3	92,372 9	74,293 0	85,801 9	80,074 2	69,827 1	63,742 3
ethane	0,107 6	2,493 6	8,065 1	1,005 3	11,002 5	5,058 3	14,151 8
propane	0,051 2	1,511 7	5,873 1	4,516 8	0,499 8	7,930 2	2,988 7
iso-butane	0,407 6	0,151 8	0,651 1	0,006 9	0,049 8	0,884 4	1,195 2
n-butane	0,012 9	0,050 3	0,148 1	0,392 2	0,640 3	1,183 2	0,892 8
neo-pentane	0,152 3	0,101 1	0,048 4	0,355 9	0,217 1	0,004 7	0,288 1
iso-pentane	0,098 4	0,277 6	0,209 2	0,348 8	0,005 0	0,050 1	0,148 9
n-pentane	0,209 3	0,281 0	0,148 7	0,007 3	0,344 8	0,049 9	0,100 5
n-hexane	0,350 7	0,282 4	0,100 1	0,148 6	0,211 4	0,005 4	0,050 1

Table A.2 — Standard uncertainty in the composition of the WMSs (% mol/mol)

	401	402	403	404	405	406	407
nitrogen	0,003 6	0,006 5	0,028 5	0,030 6	0,012 4	0,028 6	0,028 5
carbon dioxide	0,004 3	0,007 9	0,022 4	0,011 5	0,003 0	0,021 9	0,018 1
methane	0,010 8	0,016 0	0,037 2	0,033 9	0,022 3	0,038 5	0,037 1
ethane	0,003 0	0,008 2	0,021 3	0,008 3	0,019 6	0,018 7	0,030 7
propane	0,001 1	0,007 0	0,016 6	0,013 9	0,002 4	0,024 4	0,011 0
iso-butane	0,002 6	0,001 5	0,003 8	0,000 3	0,000 8	0,005 1	0,006 4
n-butane	0,000 6	0,002 6	0,002 0	0,003 1	0,004 2	0,006 6	0,005 5
neo-pentane	0,002 4	0,002 6	0,001 7	0,006 1	0,003 8	0,000 6	0,004 7
iso-pentane	0,002 4	0,003 0	0,001 9	0,003 0	0,000 6	0,000 8	0,001 8
n-pentane	0,005 2	0,003 9	0,002 0	0,000 6	0,004 2	0,000 9	0,001 5
n-hexane	0,005 7	0,004 6	0,001 8	0,002 4	0,003 4	0,000 7	0,000 9

Table A.3 — Area counts of six replicates of each of the WMSs

	Run#1	Run#2	Run#3	Run#4	Run#5	Run#6
nitrogen						
401	674 952	670 100	678 244	662 136	659 400	656 324
402	5 979 290	5 975 530	5 968 710	5 959 440	5 939 690	5 938 540
403	14 919 700	14 911 100	14 918 400	14 916 200	14 905 900	14 905 300
404	26 515 100	26 528 700	26 495 000	26 535 700	26 482 400	26 463 900
405	37 950 400	38 013 900	37 993 800	37 971 100	38 019 100	37 970 800
406	52 667 900	52 667 100	52 668 700	52 704 300	52 642 400	52 671 700
407	69 976 000	69 963 500	69 954 700	69 923 000	69 919 100	69 917 200
carbon dioxide						
401	369 630	357 800	360 700	361 980	361 660	362 730
402	10 374 900	10 378 700	10 371 500	10 367 700	10 363 600	10 373 700
403	55 707 000	55 703 300	55 766 200	55 773 800	55 741 900	55 763 900
404	20 851 500	20 848 900	20 835 800	20 878 900	20 848 500	20 853 600
405	3 561 460	3 576 990	3 570 910	3 565 540	3 571 060	3 563 420
406	42 352 500	42 351 200	42 352 300	a	42 338 800	42 348 500
407	31 596 900	31 590 600	31 602 300	31 596 100	31 597 900	31 602 000
methane						
401	465 737 000	465 398 000	465 395 000	465 731 000	465 908 000	465 617 000
402	439 578 000	439 264 000	439 248 000	439 469 000	438 906 000	439 400 000
403	358 893 000	359 013 000	359 462 000	359 320 000	359 150 000	359 600 000
404	410 119 000	410 530 000	410 044 000	410 576 000	410 405 000	410 494 000
405	384 730 000	385 486 000	385 164 000	385 261 000	385 469 000	384 975 000
406	339 398 000	339 473 000	339 401 000	339 729 000	339 289 000	339 479 000
407	312 414 000	312 471 000	312 480 000	312 470 000	312 440 000	312 396 000

a   Indicates that outliers have been removed.

Table A.3 (continued)

	Run#1	Run#2	Run#3	Run#4	Run#5	Run#6
ethane						
401	879 870	874 690	877 570	875 780	876 150	875 200
402	19 774 100	19 775 000	19 779 000	19 767 600	19 759 500	19 769 100
403	63 586 500	63 599 900	63 660 500	63 667 900	63 627 000	63 649 700
404	7 998 280	7 999 530	7 987 460	8 007 490	7 994 990	7 994 730
405	86 263 800	86 493 800	86 446 400	86 327 900	86 523 200	86 341 600
406	40 079 000	40 083 700	40 084 100	40 110 200	40 073 100	40 096 400
407	110 611 000	110 602 000	110 640 000	110 622 000	110 621 000	110 647 000
propane						
401	556 632	545 264	549 936	553 376	550 264	550 048
402	16 141 700	16 150 000	16 149 600	16 139 100	16 132 100	16 142 100
403	62 638 800	62 659 700	62 710 500	62 721 700	62 684 600	62 712 400
404	48 192 200	48 194 500	48 164 100	48 252 700	48 195 800	48 193 200
405	5 304 290	5 318 460	5 313 120	5 309 400	5 320 760	5 311 400
406	84 330 600	84 338 300	84 345 300	84 413 600	84 314 800	84 305 700
407	31 748 000	31 747 200	31 751 700	31 741 600	31 743 100	31 747 500
iso-butane						
401	4 960 830	4 953 590	4 955 070	4 961 540	4 959 560	4 956 780
402	1 837 150	1 835 020	1 834 850	1 834 500	1 835 780	1 837 620
403	7 935 690	7 938 390	7 938 040	7 943 280	7 943 730	7 944 150
404	97 416	98 384	98 152	96 952	97 496	96 952
405	599 488	602 240	600 152	595 984	598 000	601 688
406	10 705 500	10 703 900	10 709 600	10 750 000	10 737 800	10 710 600
407	14 512 400	14 511 200	14 516 500	14 506 300	14 510 600	14 511 400
n-butane						
401	142 576	139 520	139 672	144 648	142 408	142 040
402	633 824	630 312	629 696	628 344	633 088	630 936
403	1 849 800	1 853 840	1 852 580	1 850 850	1 856 780	1 854 380
404	4 990 840	4 987 510	4 985 240	4 993 070	4 994 470	4 991 550
405	8 093 580	8 112 930	8 105 380	8 088 940	8 113 500	8 103 280
406	15 045 100	15 043 200	15 050 500	15 033 000	15 016 900	15 062 400
407	11 362 200	11 363 300	11 366 900	11 357 400	11 363 000	11 362 700
neo-pentane						
401	2 010 200	2 011 950	2 015 980	2 017 630	2 015 940	2 015 460
402	1 348 430	1 346 980	1 343 940	1 343 570	1 345 900	1 343 720
403	627 624	630 424	624 824	624 360	630 400	629 016
404	4 757 860	4 760 430	4 759 850	4 762 960	4 762 610	4 755 490
405	2 894 480	2 899 460	2 897 850	2 887 990	2 899 340	2 896 540
406	55 784	52 016	56 096	54 920	58 824	54 776
407	3 853 270	3 851 560	3 853 660	3 850 050	3 848 490	3 851 260

| [a] | Indicates that outliers have been removed. |

Table A.3 *(continued)*

	Run#1	Run#2	Run#3	Run#4	Run#5	Run#6
iso-pentane						
401	1 366 070	1 363 780	1 362 080	1 373 540	1 365 270	1 360 830
402	3 840 160	3 843 790	3 839 900	3 841 500	3 844 490	3 837 380
403	2 892 860	2 897 410	2 899 990	2 902 030	2 906 300	2 901 380
404	a	4 824 380	4 824 140	4 826 060	4 824 240	4 822 820
405	76 200	77 456	78 288	75 400	75 992	76 000
406	693 416	691 672	692 328	691 208	686 456	689 288
407	2 056 740	2 062 240	2 058 390	2 054 710	2 057180	2 061 200
n-pentane						
401	2 937 110	2 929 700	2 929 880	2 935 270	2 941 930	2 931 510
402	3 947 460	3 950 370	3 945 440	3 949 300	3 954 560	3 950 380
403	2 102 140	2 110 060	2 111 660	2 110 980	2 117 560	2 105 930
404	107 768	101 776	105 336	101 320	99 512	105 312
405	4 840 860	4 857 220	4 855 860	4 846 340	4 864 450	4 849 240
406	705 992	708 224	707 752	703 384	701 320	701 432
407	1 416 060	1 423 100	1 418 580	1 413 400	1 417 500	1 421 620
n-hexane						
401	5 379 880	5 393 470	5 375 730	5 391 140	5 393 500	5 386 210
402	4 385 630	4 387 340	4 376 720	4 383 220	4 384 430	4 378 080
403	1 568 640	1 571 010	1 566 890	1 576 000	1 569 730	1 574 070
404	2 353 440	2 353 700	2 349 130	2 354 490	2 350 710	2 350 590
405	3 325 880	3 330 810	3 333 180	3 330 400	3 337 610	3 325 500
406	83 648	80 296	80 052	76 984	75 960	83 012
407	762 788	764 712	763 592	764 304	765 332	760 548

a   Indicates that outliers have been removed.

Table A.4 — Parameters of the analysis function, b_z, and of the calibration function, a_z

nitrogen - analysis function	Γ	b_0	b_1	b_2	b_3
linear	2,11	-1,479E-02	1,704E-07		
quadratic	1,40	-1,057E-02	1,683E-07	3,974E-17	
cubic	1,25	-7,215E-03	1,660E-07	1,466E-16	-1,101E-24
nitrogen - calibration function	Γ	a_0	a_1	a_2	a_3
linear	2,11	8,684E+04	5,870E+06		
quadratic	1,41	6,337E+04	5,939E+06	-7,881E+03	
cubic	1,23	4,368E+04	6,023E+06	-3,019E+04	1,340E+03
carbon dioxide - analysis function	Γ	b_0	b_1	b_2	b_3
linear	1,71	-5,696E-03	1,429E-07		
quadratic	1,33	-7,543E-03	1,435E-07	-1,488E-17	
cubic	1,15	-8,778E-03	1,441E-07	-5,424E-17	5,454E-25

Table A.4 *(continued)*

carbon dioxide - calibration function	Γ	a_0	a_1	a_2	a_3
linear	1,71	3,985E+04	6,998E+06		
quadratic	1,33	5,262E+04	6,967E+06	5,123E+03	
cubic	1,15	6,069E+04	6,939E+06	1,813E+04	-1,270E+03
methane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	1,63	-6,999E+00	2,263E-07		
quadratic	0,62	-3,903E+00	2,099E-07	2,119E-17	
cubic	0,38	-1,766E+01	3,188E-07	-2,628E-16	2,442E-25
methane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	1,63	3,092E+07	4,419E+06		
quadratic	0,61	1,931E+07	4,715E+06	-1,839E+03	
cubic	0,39	6,560E+07	2,951E+06	2,027E+04	-9,115E+01
ethane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	2,68	-6,944E-03	1,272E-07		
quadratic	0,51	-2,125E-03	1,256E-07	2,040E-17	
cubic	0,35	-2,877E-03	1,261E-07	4,253E-18	1,188E-25
ethane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	2,68	5,456E+04	7,859E+06		
quadratic	0,50	1,712E+04	7,959E+06	-9,880E+03	
cubic	0,36	2,262E+04	7,934E+06	-2,683E+03	-4,120E+02
propane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,81	-3,082E-04	9,387E-08		
quadratic	0,77	-3,582E-04	9,390E-08	-5,963E-19	
cubic	0,93	-7,580E-04	9,425E-08	-1,893E-17	1,861E-25
propane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,81	3,284E+03	1,065E+07		
quadratic	0,77	3,818E+03	1,065E+07	7,252E+02	
cubic	0,93	8,056E+03	1,061E+07	2,291E+04	-2,399E+03
iso-butane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	1,56	-9,323E-04	8,250E-08		
quadratic	1,37	-1,016E-03	8,292E-08	-4,405E-17	
cubic	0,85	-1,203E-03	8,412E-08	-3,838E-16	1,910E-23
iso-butane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	1,56	1,130E+04	1,212E+07		
quadratic	1,37	1,227E+04	1,206E+07	7,994E+04	
cubic	0,84	1,436E+04	1,188E+07	6,813E+05	-4,105E+05
n-butane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,49	1,718E-03	7,854E-08		
quadratic	0,49	1,704E-03	7,857E-08	-3,381E-18	
cubic	0,49	1,698E-03	7,860E-08	-1,039E-17	3,590E-25

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Table A.4 *(continued)*

n-butane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,49	-2,187E+04	1,273E+07		
quadratic	0,49	-2,169E+04	1,273E+07	6,984E+03	
cubic	0,49	-2,160E+04	1,272E+07	2,162E+04	-9,521E+03
neo-pentane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,43	6,610E-04	7,486E-08		
quadratic	0,30	5,556E-04	7,559E-08	-2,239E-16	
cubic	0,35	5,026E-04	7,624E-08	-7,111E-16	7,978E-23
neo-pentane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,43	-8,839E+03	1,336E+07		
quadratic	0,30	-7,329E+03	1,323E+07	5,398E+05	
cubic	0,35	-6,562E+03	1,311E+07	1,706E+06	-2,553E+06
iso-pentane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,49	-3,565E-04	7,241E-08		
quadratic	0,36	-4,818E-04	7,281E-08	-1,075E-16	
cubic	0,22	-6,514E-04	7,379E-08	-7,785E-16	1,043E-22
iso-pentane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,49	4,780E+03	1,382E+07		
quadratic	0,36	6,639E+03	1,373E+07	2,857E+05	
cubic	0,22	8,861E+03	1,355E+07	2,035E+06	-3,770E+06
n-pentane - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,41	-1,201E-04	7,097E-08		
quadratic	0,31	1,219E-05	7,056E-08	1,135E-16	
cubic	0,30	2,072E-06	7,062E-08	6,806E-17	7,333E-24
n-pentane - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,41	1,692E+03	1,409E+07		
quadratic	0,31	-1,665E+02	1,417E+07	-3,167E+05	
cubic	0,30	-4,721E+01	1,416E+07	-2,117E+05	-2,380E+05
hexanes+ - analysis function	Γ	b_0	b_1	b_2	b_3
linear	0,98	4,605E-04	6,397E-08		
quadratic	1,15	7,278E-04	6,310E-08	2,365E-16	
cubic	0,40	1,800E-04	6,644E-08	-2,141E-15	3,594E-22
hexanes+ - calibration function	Γ	a_0	a_1	a_2	a_3
linear	0,98	-7,200E+03	1,563E+07		
quadratic	1,15	-1,170E+04	1,585E+07	-9,384E+05	
cubic	0,46	-2,969E+03	1,508E+07	7,453E+06	-1,926E+07

Table A.5 — Parameters of the selected analysis function following validation

	b_0	b_1	b_2	b_3
nitrogen	-1,057 21E-02	1,683 24E-07	3,973 73E-17	0
carbon dioxide	-5,695 96E-03	1,429 04E-07	0	0
methane	-6,998 74E+00	2,263 13E-07	0	0
ethane	-2,124 65E-03	1,256 19E-07	2,039 76E-17	0
propane	-3,081 62E-04	9,386 96E-08	0	0
iso-butane	-9,323 43E-04	8,249 83E-08	0	0
n-butane	1,717 61E-03	7,853 77E-08	0	0
neo-pentane	6,610 23E-04	7,486 27E-08	0	0
iso-pentane	-3,564 78E-04	7,240 71E-08	0	0
n-pentane	-1,200 53E-04	7,096 79E-08	0	0
n-hexane	4,604 62E-04	6,396 65E-08	0	0

Table A.6 — Parameters of the selected calibration function following validation

	a_0	a_1	a_2	a_3
nitrogen	63 365,774	5 938 653,736	-7 881,0601	0
carbon dioxide	39 845,644	6 997 729,157	0	0
methane	30 924 178,877	4 418 661,180	0	0
ethane	17 122,226	7 959 319,117	-9 879,7101	0
propane	3 283,501	10 653 069,829	0	0
iso-butane	11 298,821	12 121 630,288	0	0
n-butane	-21 873,728	12 732 916,092	0	0
neo-pentane	-8 838,744	13 358 418,860	0	0
iso-pentane	4 779,839	13 815 281,180	0	0
n-pentane	1 691,842	14 090 880,066	0	0
n-hexane	-7 199,825	15 633 268,664	0	0

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Table A.7 — Hypothetical compositions employed for calculation of errors

	N_2	CO_2	CH_4	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$neo\text{-}C_5H_{12}$	$i\text{-}C_5H_{12}$	$n\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$
minimum	0,101	0,050	64,011	0,100	0,050	0,006	0,010	0,000	0,003	0,005	0,005
mean	5,970	4,027	79,970	6,396	2,347	0,481	0,435	0,007	0,136	0,122	0,109
maximum	11,999	8,000	98,463	13,998	7,996	1,200	1,200	0,034	0,350	0,350	0,350
Hypothetical compositions:											
#1	9,632	0,665	68,699	12,082	6,451	0,562	1,044	0,010	0,333	0,321	0,202
#2	1,236	7,316	69,042	13,549	6,368	0,950	0,798	0,009	0,229	0,310	0,195
:	:	:	:	:	:	:	:	:	:	:	:
:	:	:	:	:	:	:	:	:	:	:	:
#9 999	8,999	5,441	77,506	5,590	0,684	0,495	0,539	0,003	0,166	0,261	0,316
#10 000	11,363	6,199	70,801	5,157	4,124	1,164	0,754	0,011	0,222	0,159	0,044

Table A.8 — Calculated errors, and expanded uncertainties in errors, of gross calorific value

	$GCV/\mathrm{MJ \cdot m^{-3}}$	$\delta(GCV)/\mathrm{MJ \cdot m^{-3}}$	$U[\delta(GCV)]/\mathrm{MJ \cdot m^{-3}}$
minimum	30,708	-0,116	0,004
mean	38,391	0,000	0,021
maximum	47,395	0,076	0,038
Hypothetical compositions:			
#1	43,355	-0,039	0,033
#2	44,340	-0,089	0,026
,,	,,	,,	,,
,,	,,	,,	,,
#9 999	36,145	0,032	0,025
#10 000	37,133	0,053	0,031

NOTE   Uncertainties in composition and calorific value are calculated according to ISO 6974-2 and ISO 6976, as referenced in 6.6.5.

Annex B
(informative)

Explanation of approach used for instrument benchmarking

The approach adopted in this International Standard is based on the principles described in F.2.4.5 of ISO/IEC Guide 98-3:2008, which describes how a single mean correction, $\bar{b}$, may be applied to provide a best estimate of the measurand when correction from a calibration curve is not applied:

$$y'(t) = y(t) + \bar{b} \tag{B.1}$$

The mean correction, $\bar{b}$, is determined from:

$$\bar{b} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} b(t) \cdot dt \tag{B.2}$$

The single value of standard uncertainty used for all estimates $y'(t) = y(t) + \bar{b}$ of the measurand is the positive square root of

$$u_c^{\,2}(y') = \overline{u^2\left[y(t)\right]} + \overline{u^2\left[b(t)\right]} + u^2(\bar{b}) \tag{B.3}$$

The first term of Formula (B.3) is the variance of $y(t)$ due to all uncertainty sources other than $b(t)$, i.e. the uncertainty associated with the analysis of the unknown sample using the instrument.

The second term is the variance of the corrections $b(t)$ and the third term is the variance associated with the mean correction, $\bar{b}$, over the range of interest. Together, the second and third terms describe the uncertainty in the correction and, in conjunction with the mean correction, $\bar{b}$, provide the means of characterizing the performance of the instrument over the range of interest.

In the context of instrument performance evaluation, the mean error (equivalent to the mean correction in the discussion above) is computed as the mean of all errors determined for each of the N hypothetical compositions selected in 6.6.4:

$$\overline{\delta P} = \frac{\sum_{t=1}^{t=N} \delta P_t}{N} \tag{B.4}$$

where δP_t is the error (in either component amount fraction or property) calculated for the tth of N hypothetical compositions.

The standard uncertainty in mean error is determined from the positive square root of

$$u_c^{\,2}(\overline{\delta P}) = \overline{u^2\left[\delta P(t)\right]} + u^2(\overline{\delta P}) \tag{B.5}$$

where

$u^2(\overline{\delta P})$ is the variance of all errors determined for each of the N hypothetical compositions and,

$\overline{u^2\left[\delta P(t)\right]}$ is the mean of all squared uncertainties in errors determined for each of the N hypothetical compositions.

$$\overline{u^2\big[\delta P(t)\big]} = \frac{\sum_{t=1}^{t=N} u^2\big(\delta P_t\big)}{N} \tag{B.6}$$

As there is no uncertainty in the true value of the hypothetical amount fractions (and hence the properties calculated from them), the uncertainty in error, $u[\delta P(t)]$, is equal to the uncertainty in the measured amount fraction (or calculated property).

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