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Best practices in the evaluation of the measurement uncertainty of quantities relevant to fiscal measurements along the hydrogen supply chain

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Foreword

The evaluation of measurement uncertainty is a key component in any measurement. Whereas the concept *measurement uncertainty* suggests that it pertains to *measurement*, i.e., the process of experimentally obtaining one or more quantity values that can reasonably be attributed to a quantity [1, Definition 2.1], only, but in fact the necessity to evaluate and propagate this kind of uncertainty pertains to all calculations involving quantities with uncertain values. Such calculations include for instance the calculation of a calorific value from the composition of a gas, where reference data are used with given uncertainty [2–4]. The calculation does not generate any experimental data, so it is not a measurement.

The Guide to the expression of Uncertainty in Measurement (GUM) [5–10] provides a framework for evaluating and propagating measurement uncertainty, not only in measurement, but also in calculations. Energy determination in gas grids starts with measurements of, e.g., mass or volume flow rates, composition, pressure, temperature, density, calorific value and use the data thus obtained to calculate over intervals of time the mass, volume or energy supplied or delivered.

Measurement results [1, Definition 2.9] contain typically the measured value [1], or more generally, the estimate [6, Definition C.2.26] and an indication of the [6, Clause 2.2.3] measurement uncertainty. The measurement uncertainty provides information about the closeness of agreement with the true value of the quantity, which is usually unknown. Measurement uncertainty is important to assess compliance with limits, specifications, and contractual obligations [9]. The evaluation of measurement uncertainty is therefore critical in the safe operation of gas grids, as well as in trade, commerce and meeting regulatory and legislative requirements.

This best practice guide is developed within the framework of the project “Metrology for the hydrogen supply chain” to provide novel methods for the evaluation of measurement uncertainty along the supply chain as a whole, namely with regard to the measurement of total quantity, and energy and impurity content of hydrogen and hydrogen blends. The document supplements existing guidance on the evaluation of measurement uncertainty, fiscal metering and international standards in this area. It is intended to support the industry and users of other standards to enhance their practices in evaluating measurement uncertainty by including the dependencies between the quantities involved, as well as the dynamics in such gas grids into these evaluations, to provide realistic uncertainty budgets for the relevant quantities.

The guidance provided in this document is provided in good faith. It is provided “as is” without any warranty or that it is fit for a particular purpose.

Table of contents

Introduction

The transition from fossil fuels to renewable fuels is reflected in an increase of the production and use of biogas, biomethane and hydrogen from renewable sources. To increase the production of these renewable energy gases, their use should increase too, which calls for transmission and distribution systems that are ready to receive and supply them. To an extent, current natural gas infrastructure is used for this purpose alongside the construction of distribution systems for hydrogen only. The transmission system operators (TSOs) and distribution system operators (DSOs) see also the geometry of their grids change, in particular with respect to the number of points where gas enters their grids.

The use of a greater diversity of gaseous fuels also creates larger fluctuations in the properties measured for billing and custody transfer. These larger fluctuations are caused by a greater diversity of gaseous fuels transmitted and distributed through gas grids. Another cause lies in the fact that the production of biomethane and hydrogen from renewable sources is usually taking place at a smaller scale than the production of natural gas, which leads to a more distributed supply of these renewable energy gases, leading to a larger number of entry points.

A concern from TSOs and DSO is that current practices such as those described in ISO 15112 [11], EN 1776 [12] and OIML R140 [13] no longer suffice to evaluate in a reliable manner fiscal metering data, including the evaluation of measurement uncertainty. Said documents consider the measurement results that enter into the calculation of total volume, mass or energy as mutually independent. Failing to address these dependencies severely underrates the uncertainty calculated for total quantity and total energy.

This best practice guide describes novel methods for the evaluation of measurement uncertainty along the supply chain, namely with regard to the measurement of total quantity, and energy and impurity content of hydrogen and hydrogen blends. These methods address the correlations arising due to (1) the use of the same instrumentation for the measurement result, (2) temporal (serial correlation) effects, and (3) effects arising from the use of time averages. These novel methods find their root in the methods of the Guide to the expression of Uncertainty in Measurement (GUM).

Whereas the framework of the GUM is deemed to be generally applicable [6], it is only so for measurement models where there are no constraints between the input quantities. Thus, for measurement models that have as input the composition of the fuel gas, the framework was extended to provide appropriate sensitivity coefficients for using the law of propagation of uncertainty (LPU) [6, 8]. The Monte Carlo method (MCM) that can also be used for propagating measurement uncertainty is less affected by this issue, if the constraint on the amount fractions forming the composition is duly respected [14].

The guidance is aimed at specialists in gas metering, members of standardisation committees and developers of software to support fiscal metering, billing, custody transfer and gas allocation.

1 Scope

1.1 This best practice guide describes approaches for the evaluation of measurement data of gaseous fuels, such as natural gas, biomethane, hydrogen and blends thereof. The guidance supplements existing guidance such as provided in ISO 15112, OIML R140 and other documents concerned with the metering of gas to obtain a total quantity or energy supplied or received. The intent of these measurements is to enable financial transactions, such as those between buyer and seller, conformity assessment with respect to regulatory and contractual requirements and taxation.

1.2 This guide describes best practices in evaluating the measurement uncertainty, building forth on the principles of and guidance in the Guide to the expression of Uncertainty in Measurement (GUM). It supplements and goes beyond the guidance in e.g., ISO 15112 [11] and OIML R140 [13] as this guide considers the dependencies between quantities as they arise in fiscal metering and includes them when propagating measurement uncertainty.

This guide uses the framework of the GUM, which is based on

(a) the specification of the measurand (quantity of interest),

(b) the formulation of a measurement model,

(c) the evaluation of the uncertainty of the input variables in that model and

(d) using a suitable mechanism to propagate the measurement uncertainty from the input quantities to the output quantities of the measurement model.

Notwithstanding that most of the guidance is written with the law of propagation of uncertainty (LPU) in mind, the guidance in this document can equally well be applied when using the Monte Carlo method (MCM). As the LPU is the industry standard in these evaluations, it is used predominantly in this guide.

1.3 This guide uses, where appropriate, vector and matrix algebra. Whereas on one hand this notation is not perceived as the most accessible under physicists, chemists and engineers, yet it is in many instances much simpler to implement in software than their counterparts without using vectors and matrices. It should be born in mind that matrix multiplications and transpositions, the commonest operations, are also available in mainstream spreadsheet software.

2 Normative references

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

ISO/IEC Guide 98-3 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995). ISO, International Organization for Standardization, Geneva, Switzerland, 2008. First edition

ISO/IEC Guide 98-3:2008/Suppl 1:2008 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995) — Supplement 1: Propagation of distributions using a Monte Carlo method. ISO, International Organization for Standardization, Geneva, Switzerland, 2008. First edition

ISO/IEC Guide 98-3:2008/Suppl 2:2011 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995) — Supplement 2: Extension to any number of output quantities. ISO, International Organization for Standardization, Geneva, Switzerland, 2011. First edition

ISO/IEC Guide 98-6 Uncertainty of measurement — Part 6: Developing and using measurement models. ISO, International Organization for Standardization, Geneva, Switzerland, 2021. First edition

ISO 6974–1 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 1: Guidelines for tailored analysis. ISO, International Organization for Standardization, Geneva, Switzerland, 2012. Second edition

ISO 6974–2 Natural gas — Determination of composition with defined uncertainty by gas chromatography — Part 2: Measuring-system characteristics and statistics for processing of data. ISO, International Organization for Standardization, Geneva, Switzerland, 2012. Second edition

ISO 6976 Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition. ISO, International Organization for Standardization, Geneva, Switzerland, third edition, 2016

ISO 15112 Natural gas — Energy determination. ISO, International Organization for Standardization, Geneva, Switzerland, 2018. Third edition

ISO 20765-2 Natural gas — Calculation of thermodynamic properties — Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application. ISO, International Organization for Standardization, Geneva, Switzerland, 2008. First edition

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO/IEC Guide 98-3:2008, ISO/IEC Guide 98-3/Supplement 1:2008, ISO/IEC Guide 98-3/Supplement 2:2011, ISO/IEC Guide 99:2007, ISO 14532 and the following apply.

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

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

3.1
relative standard uncertainty

absolute value of the quotient of the standard uncertainty and the associated measured value

NOTE The relative standard uncertainty is not defined if the measured value is zero.

3.2
relative expanded uncertainty

absolute value of the quotient of the expanded uncertainty and the associated measured value

NOTE The relative expanded uncertainty is not defined if the measured value is zero.

3.3
uncertainty budget

list of sources of measurement uncertainty, their method of evaluation, sensitivity coefficients, standard uncertainties and covariances used in an uncertainty evaluation

3.4
time series

series of data points indexed by their time of observation

3.5
autocorrelation
serial correlation

dependence of a data point in a time series on its predecessor or predecessors

3.6
autocovariance function

mathematical function providing the covariance due to autocorrelation in a time series

3.7
autocorrelation function

mathematical function providing Pearson’s correlation coefficient due to autocorrelation in a time series

3.8
partial correlation

correlation between two random variables with the linear effect of other variables removed.

3.9
partial autocorrelation function

mathematical function providing the autocorrelation in a time series with the linear dependence of terms between the two observations being analysed removed

3.10
weakly stationary time series

finite-variance process such that

i) the mean is constant and does not depend on time;

ii) the autocovariance function depends only on the distance between two observations and not on time.

3.11
(purely) random process

process such that any of its realizations is a sequence of mutually independent and identically distributed variables.

3.12
autoregressive process

finite-variance process X_t such that

$$X_t = \alpha_1 X_{t-1} + \cdots + \alpha_p X_{t-p} + Z_t$$

where $\alpha_1, \ldots, \alpha_p$ are constants and Z_t is a purely random process. p is called the order of the autoregressive process.

3.13
moving average process

finite-variance process X_t such that

$$X_t = \beta_0 Z_t + \beta_1 Z_{t-1} + \cdots + \beta_q Z_{t-q}$$

where $\beta_0, \ldots, \beta_q$ are constants and Z_t is a purely random process. q is called the order of the moving average process.

4 General principles

4.1 Measurement model

4.1.1 Measurement uncertainty is propagated using a measurement model. An explicit measurement model with one output quantity is denoted by

$$Y = f(X_1, \ldots, X_N) \tag{1}$$

where Y denotes the output quantity of the measurement model, f the functional relationship and $X_1, \ldots, X_N$ the N input quantities. The output quantity is also called the measurand.

4.1.2 A measurement model should be developed in such a fashion that it includes all variables that affect the uncertainty of the output quantity in a meaningful way. ISO/IEC Guide 98-6:2021 [10] provides guidance on developing measurement models. Where necessary, this guidance is applied in this guide to extend models used in fiscal metering to make these suitable for the propagation of measurement uncertainty.

4.1.3 The input quantities $X_1, \ldots, X_N$ should be evaluated as part of an evaluation of measurement uncertainty. Depending on the information about them, type A methods of uncertainty evaluation or type B methods can be employed. Type A methods involve the use of statistical methods for data reduction, including analysis of variance, regression and time series analysis (see also clause 11). Type B methods on the other hand use other information to elicit a probability density function, which describes the knowledge about that input quantity. In this guide, in most instances this probability density function is a normal distribution or rectangular distribution.

4.1.4 An input quantity of a measurement model can also have been an output quantity of a measurement model in a preceding uncertainty evaluation. In that case, the input quantity is evaluated using the measurement model of that preceding stage. In this guide, this mechanism is often used, as in the measurement of the total quantity (e.g., mass, volume) or energy, the measurement results of, e.g., measurements of the flow rate and calorific value are used. The measurement results of these flow rates and calorific values are obtained using their own measurement models.

In many instances, a measurement model has multiple output quantities, which is the multivariate pendant of equation (1), viz.,

$$\begin{aligned} Y_1 &= f_1(X_1, \ldots, X_N) \\ &\cdots \\ Y_M &= f_M(X_1, \ldots, X_N) \end{aligned} \tag{2}$$

which can be written in vector-matrix notation as

$$\boldsymbol{Y} = \boldsymbol{f}(\boldsymbol{X}) \tag{3}$$

where $\boldsymbol{Y} = [Y_1, \ldots, Y_M]^\top$, $\boldsymbol{f} = [f_1, \ldots, f_M]^\top$, and $\boldsymbol{X} = [X_1, \ldots, X_N]^\top$.

4.2 Evaluation of uncertainty of input quantities

4.2.1 Unless otherwise stated, this guide assumes that measured natural gas properties, such as amount fractions of components, calorific values, volumes, masses can be modelled using the normal distribution. It is assumed that measurement equipment is calibrated, and calibration gas mixtures used to calibrate (on-line) analysers are accompanied by an appropriate calibration or reference material certificate [16].

4.2.2 For the uncertainty sources, this guide follows the guidance of ISO/IEC Guide 98-3:2008 and ISO/IEC Guide 98-3/Supplement 1:2008 [6, 7] with regard to the selection of probability density functions (PDFs) for input quantities.

4.2.3 Where input quantities are correlated, which is usually the case for those quantities measured periodically in gas metering stations, a joint PDF is chosen with an appropriate vector of values and associated covariance matrix.

NOTE In legal metrology, the uncertainty arising from using a measuring instrument is often modelled using a rectangular distribution and a maximum permissible error (MPE) [13].

4.3 Propagation of measurement uncertainty

4.3.1 This guide applies, when using the LPU, the process described in ISO/IEC Guide 98-3:2008 clause 8 [6], or, in the case of a multivariate or implicit measurement model, the process described in ISO/IEC Guide 98-3/Supplement 2:2011 clause 6.3 [8].

4.3.2 When using the propagation of distributions, also known as the MCM, this guide uses the process described in ISO/IEC Guide 98-3/Supplement 1:2008 clause 7 [7] and in the case of a multivariate measurement model ISO/IEC Guide 98-3/Supplement 2:2011 clause 7 [8].

4.3.3 Covariances between input quantities are included in the uncertainty evaluations, either by making these dependencies explicit in the measurement models used, or by assigning multivariate probability density functions to sets of input quantities [8, clause 5.3].

4.3.4 This guide takes the view that dependencies between variables should be evaluated to perform a proper evaluation of measurement uncertainty. Where these dependencies are ignored by setting the correlation coefficient, or equivalently, the covariance to zero, such decision should be corroborated by an assessment.

4.3.5 The LPU should in principle only be used for nearly linear measurement models [10]. Many of the measurement models used in fiscal metering of energy gases are distinctively non-linear which may cause that the linear approximation underlying the LPU is insufficient to produce a reliable estimate (value) and associated uncertainty. If there is doubt about using the LPU, the uncertainty evaluation should be validated using the MCM from ISO/IEC Guide 98-3/Supplement 1:2008 [7] or for multivariate measurement models its extension from ISO/IEC Guide 98-3/Supplement 2:2011 [8].

4.4 Law of propagation of uncertainty

4.4.1 When propagating measurement uncertainty, it is important to know whether the input quantities are independent. Independence is the case when one variable does not influence the value, and thus the PDF, of the other. Dependencies between quantities arise, e.g., when two quantities depend on a joint third one.

4.4.2 In fiscal metering of energy gases, often the same instruments are used to obtain a (large) series of measurement results. These results are all dependent by nature, as they share several contributions in their uncertainty budgets. Guidance on evaluating such dependencies is given in clauses 6, 7, 8 9 and 10.

4.4.3 On the other hand, when constructing a measurement model [10], often an attempt is made to come up with a form in which the input quantities are mutually independent, as it makes their evaluation easier as well as the propagation of measurement uncertainty.

4.4.4 When the input quantities $X_1, \ldots, X_N$ are mutually independent or uncorrelated, the variance of the output quantity can be computed as [6, equation (10)]

$$u^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \tag{4}$$

where

$$c_i = \frac{\partial f}{\partial x_i} \tag{5}$$

is called the sensitivity coefficient. It is the first partial derivative of f with respect to X_i evaluated at $X_i = x_i$. The product [6, clause 5.1.3]

$$u_i(x_i) = c_i u(x_i) \tag{6}$$

is called uncertainty contribution. For a measurement model with mutually independent quantities, $u(y)$ is obtained as the square root of the sum of the squared uncertainty contributions $u_i(x_i)$, $i = 1, \ldots, N$. The list of uncertainty contributions is called an uncertainty budget [17].

4.4.5 In this guide, sensitivity coefficients are often obtained using symbolic differentiation. For using the LPU, a simple formula for the partial derivative is not required. Instead, numerical differentiation techniques can be used as well [14, 18]. For example, the functional relationship between the input and output quantities in many equations of state is quite involved and not so easy to handle using symbolic differentiation. In these instances, this guide will use numerical methods. These methods can of course also be used where symbolic differentation is used.

4.4.6 For simple sums, differences, products and quotients, the variance of the output quantity can be readily expressed in terms of the input quantities. As these equations are frequently used throughout this guide, they are given here for convenience.

Given $y = x_1 + x_2$, then

$$u^2(y) = u^2(x_1) + u^2(x_2)$$

Given $y = x_1 - x_2$, then

$$u^2(y) = u^2(x_1) + u^2(x_2)$$

Given $y = x_1 x_2$, then

$$\frac{u^2(y)}{y^2} = \frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2}$$

Given $y = x_1/x_2$, then

$$\frac{u^2(y)}{y^2} = \frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2}$$

These expressions for simple sums, differences, products and quotients can be readily extended to more than two input quantities.

4.4.7 If there are correlations between pairs of input quantities in the set $X_1, \ldots, X_N$, then covariances should be taken into account. In that instance, the variance of the output quantity y is given by [6, equation (13)]

$$u^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j) \tag{7}$$

where $u(x_i, x_j)$ is the covariance between x_i and x_j. The double summation runs over all combinations of dependent input quantities.

Note that when working with covariances, it is essential to carry the signs of the sensitivity coefficients and of the covariances!

4.4.8 For *dependent* input quantities, the same four basic formulæ for calculating the variance of a sum, difference, product and quotient can be developed.

Given $y = x_1 + x_2$, then

$$u^2(y) = u^2(x_1) + u^2(x_2) + 2r(x_1, x_2)u(x_1)u(x_2)$$

Given $y = x_1 - x_2$, then

$$u^2(y) = u^2(x_1) + u^2(x_2) - 2r(x_1, x_2)u(x_1)u(x_2)$$

Given $y = x_1 x_2$, then

$$\frac{u^2(y)}{y^2} = \frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2} + 2\frac{1}{x_1 x_2} r(x_1, x_2)u(x_1)u(x_2) \tag{8}$$

NOTE The proof is as follows. From the measurement equation, it follows

$$\mathrm{d}y = x_2\,\mathrm{d}x_1 + x_1\,\mathrm{d}x_2$$

Dividing both sides by $y = x_1 x_2$,

$$\frac{\mathrm{d}y}{y} = \frac{\mathrm{d}x_1}{x_1} + \frac{\mathrm{d}x_2}{x_2}$$

Given $y = x_1/x_2$, then

$$\frac{u^2(y)}{y^2} = \frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2} - 2\frac{1}{x_1 x_2} r(x_1, x_2)u(x_1)u(x_2)$$

NOTE The proof is as follows. From the measurement equation, it follows

$$\mathrm{d}y = \frac{1}{x_2}\,\mathrm{d}x_1 - \frac{x_1}{x_2^2}\,\mathrm{d}x_2$$

Dividing both sides by $y = x_1/x_2$,

$$\frac{\mathrm{d}y}{y} = \frac{\mathrm{d}x_1}{x_1} - \frac{\mathrm{d}x_2}{x_2}$$

Extension of these expressions to more than two variables can be performed. It is important to recall that for every *combination* of dependent input quantities a covariance term appears. So, if X_1, X_2, X_3 are the input quantities and they are mutually dependent, then there are three covariances to be included, $u(x_1, x_2)$, $u(x_1, x_3)$ and $u(x_2, x_3)$.

4.5 Sensitivity coefficients

4.5.1 Sensitivity coefficients are often obtained using symbolic differentiation. That method is also widely used in this document.

4.5.2 Measurement models that have a chemical composition as one of the arguments require special attention when used with the LPU from the GUM. The constraint that the amount fractions in a composition add to unity exactly (see equation (55)) does not only affect the covariance matrix associated with the composition, but also impacts the differentiation of the measurement model to obtain the expressions and values of the sensitivity coefficients, as differentiating the model with respect to each variable individually and independently may not be possible as it may involve evaluating the model for infeasible inputs leading to an undefined output.

4.5.3 Neither ISO/IEC Guide 98-3:2008 nor ISO/IEC Guide 98-3/Supplement 2:2011 [6, 8], provide any guidance on how to deal with the specifics of such measurement models. Mathematical functions with probabilities [19], compositions and the like require an approach with respect to partial differentiation that is markedly different from functions where there are no constraints on the arguments. The response of the measurement model to a (finite) change in the input quantities is usually different when the constraint is considered from that of the measurement model taking the input quantities as independent.

EXAMPLE Consider the model from ISO 6976 [4] for calculating the molar calorific value H from the pure component calorific values $h_1, \ldots, h_N$ for a mixture with N components with amount fractions $x_1, \ldots, x_N$

$$H = \sum_{j=1}^{N} x_i h_i \tag{9}$$

The partial derivatives with respect to h_i are obtained as usual,

$$\frac{\partial H}{\partial h_i} = x_i \tag{10}$$

whereas those with respect to x_i should be obtained respecting the normalisation constraint (see clause 8.4.2) [14, 19]

$$\frac{\partial H}{\partial x_i} = h_i - \bar{h} \tag{11}$$

where

$$\bar{h} = \frac{1}{N} \sum_{i=1}^{N} h_i$$

The expression for the sensitivity coefficients with respect to x_i are notably different from the ones obtained without respecting the constraint.

NOTE 1 ISO 6976 [4] provides the same output uncertainties for the molar calorific value, molar mass and compressibility factor (and related quantities) if a covariance matrix is used which satisfies the normalisation constraint [20, 21].

NOTE 2 The sensitivity coefficients provided by equation (11) describe the physical reality; the smaller the differences between the pure component calorific values, the smaller the uncertainty contribution due to the composition becomes. In the case of the molar mass of isomers (i.e., components with the same molar mass), there is no uncertainty contribution due to the composition, for the molar masses of isomers (e.g., the pentanes) are usually taken as identical.

NOTE 3 The partial derivatives given in equations (10) and (11) can be obtained numerically.

NOTE 4 The constrained partial derivatives are unique [14, 19].

4.5.4 Given a function f with as one of the arguments a composition $\boldsymbol{x}$, the derivatives with respect to the components in the composition can be obtained as follows. Let us assume that f is differentiable on the domain of $\boldsymbol{x}$. Further, the constraint of equation (55) can be formulated as [19]

$$g(\boldsymbol{x}) = \sum_{i=1}^{N} x_i - 1 = 0 \tag{12}$$

The Jacobian of a scalar function f is defined as a row vector with as elements $j = 1, \ldots, N$ [22]

$$J_j = \frac{\partial f}{\partial x_j} \tag{13}$$

but now considering that the x_j are dependent through the normalisation constraint. From the definition of a derivative, let us define a directional derivative $f'_{\boldsymbol{q}}$ at $\boldsymbol{x} = \boldsymbol{x_0}$ as

$$f'_{\boldsymbol{q}}(\boldsymbol{x_0}) = \lim_{h \to 0} \frac{f(\boldsymbol{x_0} + h\boldsymbol{q}) - f(\boldsymbol{x_0})}{h} \tag{14}$$

where it is required that $\boldsymbol{x_0} + h\boldsymbol{q}$ is also a valid composition for a sufficiently small h. In this case, the constraint (12) can be expressed as $g(\boldsymbol{x}) = \boldsymbol{e}^\top \boldsymbol{x} - 1 = 0$ where $\boldsymbol{e}^\top = (1, \ldots, 1)$. $\boldsymbol{x_0} + h\boldsymbol{q}$ is a valid composition if $\boldsymbol{q}$ is orthogonal to $\boldsymbol{e}$. From the requirement that $\boldsymbol{x_0} + h\boldsymbol{q}$ is a valid composition, it follows that the sum of the elements in $\boldsymbol{q}$ is zero.

4.5.5 The relationship between a directional derivative $f'_{\boldsymbol{q}}$ and the Jacobian J is

$$f'_{\boldsymbol{q}} = J\boldsymbol{q} \ . \tag{15}$$

A finite value for h will be used instead of computing the limit in equation (14) [14].

4.5.6 The vectors $\boldsymbol{q}$ can be obtained in different ways. These start with computing an orthogonal matrix with $N-1$ columns and N rows. The columns hold the vectors $\boldsymbol{q}$ of the directional derivatives. The matrix Q for a composition with N components can be formed as follows [14]. For each column $j = 1, \ldots, N-1$, the first j elements are equal to

$$\frac{-1}{\sqrt{j(j+1)}} \tag{16}$$

and the following element is equal to

$$\frac{j}{\sqrt{j(j+1)}} \tag{17}$$

The remaining elements are zero.

EXAMPLE For $N = 5$, using equations (16) and (17)

$$Q = \begin{bmatrix} -0.70711 & -0.40825 & -0.28868 & -0.22361 \\ 0.70711 & -0.40825 & -0.28868 & -0.22361 \\ 0 & 0.81650 & -0.28868 & -0.22361 \\ 0 & 0 & 0.86603 & -0.22361 \\ 0 & 0 & 0 & 0.89443 \end{bmatrix} \tag{18}$$

For each of the columns $\boldsymbol{q}_j$ in Q, compute

$$b_j = \frac{f(\boldsymbol{x_0} + h\boldsymbol{q}_j) - f(\boldsymbol{x_0})}{h}. \tag{19}$$

Then the sensitivity coefficients are given by [14]

$$\boldsymbol{c}^\top = \boldsymbol{b}Q^\top. \tag{20}$$

NOTE The ISO/IEC Guide 98-3:2008 and ISO/IEC Guide 98-3/Supplement 2:2011 [6, 8] presume that partial derivatives are computed symmetrically about the estimate. To do so, instead of equation (19), the following approximation for the directional derivative can be used instead

$$b_j = \frac{f(\boldsymbol{x}_0 + h\boldsymbol{q}_j) - f(\boldsymbol{x}_0 - h\boldsymbol{q}_j)}{2h}. \tag{21}$$

Using equation (21) instead of equation (19) comes at the computational expense of N extra calls to the measurement equation f.

4.5.7 According to the guidance in ISO/IEC Guide 98-3:2008 [6, clause 5.1.3 NOTE 2], h can be chosen in the order of a standard uncertainty. For natural gas compositions, the standard uncertainties can be substantially different between the most abundant component (methane) and minor components such as the pentanes and hexane. A practical choice is to take 1 % of the smallest amount fraction in the composition, which will ensure both satisfactory performance for the minor components and a valid composition for $\boldsymbol{x_0} \pm h\boldsymbol{q}$.

4.5.8 The approximation of the partial derivatives for input quantities that are not subject to a constraint can be performed in the usual way, i.e., by directly approximating the partial derivative using a finite difference.

EXAMPLE Equations of state are usually a function of the composition, temperature and pressure. The latter two quantities are not subject to a constraint, so their partial derivatives can be approximated using the process from ISO/IEC Guide 98-3:2008 [6, clause 5.1.3 NOTE 2]. So, evaluating the equation of state for $\boldsymbol{x_0}, T + \delta T, p$ and a second time for $\boldsymbol{x_0}, T, p + \delta p$, enables evaluating these two partial derivatives, which are approximated by

$$\frac{\partial f}{\partial T} = \frac{f(\boldsymbol{x_0}, T + \delta T, p) - f(\boldsymbol{x_0}, T, p)}{\delta T}, \tag{22}$$

and

$$\frac{\partial f}{\partial p} = \frac{f(\boldsymbol{x_0}, T, p + \delta p) - f(\boldsymbol{x_0}, T, p)}{\delta p}. \tag{23}$$

In these expressions, $\boldsymbol{x_0}$ denotes the input composition, whereas f denotes the equation of state.

NOTE 1 The numerical methods for obtaining the sensitivity coefficients described in this clause enable propagating the measurement uncertainty from the measurement of composition, pressure and temperature through an equation of state.

NOTE 2 Even if the measurement model is implicit [8] or an algorithm, the numerical approximations can be used with an implementation that delivers the relevant output quantity or quantities as a function of the input quantities.

NOTE 3 In clause 9, the gradient (i.e., the partial derivatives ignoring the constraint) are used. The proof that these partial derivatives provide the same results when the covariance matrix associated with the composition is properly formed [21] is given elsewhere [14].

4.6 Monte Carlo method

4.6.1 Dependencies between input quantities in measurement models can be handled with the MCM as well. With regard to dependencies between input quantities, these are modelled using a joint PDF that describes not only the knowledge about the input quantities themselves, but also their interdependencies. In the case of input quantities modelled by normal distributions, the joint PDF is a multivariate normal distribution that takes as arguments a vector with the means of the input quantities and a covariance matrix providing the squared standard uncertainties and covariances [7, 8].

4.6.2 Dependencies can also be articulated in the measurement model by providing explicitly the mathematical relationships between the input quantities.

4.7 Evaluating covariances

4.7.1 The evaluation of covariances using type A methods of evaluating measurement uncertainty is well known. The calculation of the sample covariance of a series of observations (x_{1j}, x_{2j}) is carried out as follows [6, clause 5.2.3]

$$u(\bar{x}_1, \bar{x}_2) = \frac{1}{n-1}\sum_{j=1}^{n}(x_{1j} - \bar{x}_1)(x_{2j} - \bar{x}_2) \tag{24}$$

where

$$\bar{x}_1 = \frac{1}{n}\sum_{j=1}^{n} x_{1j}; \quad \bar{x}_2 = \frac{1}{n}\sum_{j=1}^{n} x_{2j}. \tag{25}$$

The correlation coefficient and the covariance are related as follows [6, clause 5.2.2]

$$u(x_1, x_2) = r(x_1, x_2)u(x_1)x(x_2) \tag{26}$$

where $r(x_1, x_2)$ denotes the correlation coefficient between x_1 and x_2. Correlation coefficients take values in the interval $[-1, 1]$. If a correlation coefficient is zero, then the pair of variables is uncorrelated [23]. Whereas covariances and variances enter into the LPU, for expressing information about uncertainty correlation coefficients and standard uncertainties are more readily interpretable. Hence, the latter will be used for this purpose.

4.7.2 If the input quantities X_i and X_j depend on a set of quantities Q_ℓ, $\ell = 1,\dots,L$, then [6, equationn (F.2)]

$$u(X_i,X_j) = \sum_{\ell=1}^{L} \frac{\partial X_i}{\partial Q_\ell}\frac{\partial X_j}{\partial Q_\ell} u^2(Q_\ell) \tag{27}$$

where it is assumed that the Q_ℓ are mutually independent.

NOTE Equation (27) can be viewed as the sum of the products of the uncertainty contributions to X_i and X_j for the input quantities Q_ℓ for $\ell = 1,\dots,L$. Note that an uncertainty contribution is zero if the output quantity does not depend on the input quantity in question. In that case, the corresponding sensitivity coefficient is zero.

4.7.3 Whereas equation (27) holds if the values of $u(Q_\ell)$ for X_i and X_j are the same, in many uncertainty budgets the modelled effect is correlated, but the values of the standard uncertainty are different. Let the standard uncertainties be denotes by $Q_{i\ell}$ and $Q_{j\ell}$ for X_i and X_j respectively, then

$$u(X_i,X_j) = \sum_{\ell=1}^{L} \frac{\partial X_i}{\partial Q_\ell}\frac{\partial X_j}{\partial Q_\ell} u(Q_{i\ell})u(Q_{j\ell}) \tag{28}$$

where it is assumed, like in equation (27), that the correlation coefficient is one.

EXAMPLE In the use of a temperature transmitter, the influence of the ambient temperature on the performance of the transmitter is modelled as a function of the ambient temperature. Hence, when evaluating the covariance between two temperature measurements made at different ambient temperatures, the standard uncertainties due to this effect will generally be different. With equation 28, the contribution to the covariance can be readily evaluated.

4.8 Multivariate measurement models

4.8.1 A limitation of equation (27) is that it requires the input quantities $Q_1,\dots,Q_L$ to be mutually independent. In this guide, measurement models are used where this limitation is no restriction, but in particular in the models that take a chemical composition as input, this restriction is an issue. Notwithstanding that there is a counterpart for equation (27) that works with *dependent* input quantities [24], it is more practical to work in this instance with multivariate measurement models. The extension of ISO/IEC Guide 98-3:2008 and ISO/IEC Guide 98-3/Supplement 1:2008 to multivariate measurement models provides a versatile way of propagating measurement uncertainty from one measurement model to another.

4.8.2 When dealing with correlated input quantities, it can be advantageous to formulate the measurement models as multivariate measurement models, viz., [8, clause 5.1.2]

$$\begin{aligned} Y_1 &= f_1(X_1,\dots,X_N) \\ &\dots \\ Y_M &= f_M(X_1,\dots,X_N) \end{aligned}$$

The measurement model can be written as

$$\boldsymbol{Y} = \boldsymbol{f}(\boldsymbol{X}) \tag{29}$$

where $\boldsymbol{Y}^\top = (Y_1, \ldots, M)$, $\boldsymbol{f}^\top = (f_1, \ldots, f_M)$ and $\boldsymbol{X} = (X_1, \ldots, X_N)$. The LPU can be written as [8, clause 6.2.1]

$$\boldsymbol{V_y} = \boldsymbol{C_x} \boldsymbol{V_x} \boldsymbol{C_x}^\top \tag{30}$$

where $\boldsymbol{V_y}$ is the covariance matrix associated with $\boldsymbol{Y}$, $\boldsymbol{C}$ the sensitivity matrix, and $\boldsymbol{V_x}$ the covariance matrix associated with $\boldsymbol{X}$, viz.,

$$\boldsymbol{V_x} = \begin{bmatrix} u^2(x_1) & \cdots & u(x_1, x_N) \\ \vdots & \ddots & \vdots \\ u(x_N, x_1) & \cdots & u^2(x_N) \end{bmatrix}$$

and

$$\boldsymbol{C} = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \cdots & \dfrac{\partial f_1}{\partial x_N} \\ \vdots & \ddots & \vdots \\ \dfrac{\partial f_M}{\partial x_1} & \cdots & \dfrac{\partial f_M}{\partial x_N} \end{bmatrix}$$

4.8.3 Defining the correlation matrix as

$$\boldsymbol{R_x} = \begin{bmatrix} 1 & \cdots & r(x_1, x_N) \\ \vdots & \ddots & \vdots \\ r(x_N, x_1) & \cdots & 1 \end{bmatrix}$$

where r denotes the correlation coefficient and considering that $r(x_i, x_i) = 1$, the relationship between the correlation matrix and covariance matrix is [8, clause 3.21]

$$\boldsymbol{V_x} = \boldsymbol{D} \boldsymbol{R_x} \boldsymbol{D}$$

where $\boldsymbol{D} = \mathrm{diag}\{u(x_1), \ldots, u(x_N)\}$. Using this relationship, the LPU for multivariate measurement models can be written as

$$\boldsymbol{V_y} = \boldsymbol{C_x} \boldsymbol{D} \boldsymbol{R_x} \boldsymbol{D} \boldsymbol{C_x}^\top \tag{31}$$

4.8.4 The correlation matrix can be calculated from the covariance matrix as follows [8, definition 3.21]

$$\boldsymbol{R_x} = \boldsymbol{D}^{-1} \boldsymbol{V_x} \boldsymbol{D}^{-1}$$

where $\boldsymbol{D}^{-1} = \mathrm{diag}\{u^{-1}(x_1), \ldots, u^{-1}(x_N)\}$.

NOTE For a univariate, explicit measurement model (see equation (1)), the variance of the output quantity in vector-matrix notation can be written as

$$u^2(y) = \boldsymbol{C_x} \boldsymbol{V_x} \boldsymbol{C_x}^\top$$

where

$$\boldsymbol{C_x} = \left[\frac{\partial f}{\partial x_1}, \ldots, \frac{\partial f}{\partial x_N} \right]$$

4.9 Reporting

4.9.1 Measurement results shall be reported in accordance with the requirements of ISO/IEC Guide 98-3:2008 [6, clause 7]. In this guide, generally standard uncertainties are provided with two decimal figures, and the associated values (estimates) are rounded accordingly.

4.9.2 When reporting results with dependencies, it can be necessary to use more than two decimal figures for the standard uncertainties [18, clause 6].

NOTE General requirements with respect to reporting measurement results are given in ISO/IEC 17025 [16, clause 7.8].

5 Total energy and quantity measurement

5.1 Mass

5.1.1 The mass of gas delivered over a time period is calculated by summing the measured mass flow rates of a time interval, i.e.,

$$m(t_j) = \Delta t \sum_{i=0}^{j} \dot{m}_i \tag{32}$$

where it is assumed that the flow rate measurements are made at regular time intervals Δt.

NOTE Equation (32) is an approximation of the integration the continuous function of the mass flow rate over the time interval of interest. This approximation has also an uncertainty, which can be evaluated as described in clause 13.

5.1.2 As far as it concerns the effect of the measurement, the standard uncertainty associated with $m(t_j)$ can be readily obtained using the LPU for correlated input quantities [6, eqn. (13)], or, alternatively, the LPU for multivariate measurement models from ISO/IEC Guide 98-3/Supplement 2:2011 [8].

5.1.3 The uncertainty associated with Δt in summations like equation (32) can be ignored, as its uncertainty is negligible in comparison to the uncertainties associated with the other quantities in the measurement model.

5.1.4 Using the LPU for correlated input quantities, the expression for the squared standard uncertainty associated with the mass $m(t_j)$ is given by

$$u^2(m(t_j)) = (\Delta t)^2 \sum_{i=0}^{j} u^2(\dot{m}_i) + 2(\Delta t)^2 \sum_{i=0}^{j} \sum_{k=i+1}^{j} u(\dot{m}_i, \dot{m}_k) \tag{33}$$

or, using correlation coefficients,

$$u^2(m(t_j)) = (\Delta t)^2 \sum_{i=0}^{j} u^2(\dot{m}_i) + 2(\Delta t)^2 \sum_{i=0}^{j} \sum_{k=i+1}^{j} r(\dot{m}_i, \dot{m}_k) u(\dot{m}_i) u(\dot{m}_k) \tag{34}$$

NOTE Guidance on how to evaluate the standard uncertainties associated with the flow rates and the correlation coefficients is given in clause 10 of this guide.

5.2 Volume

5.2.1 The volume of gas delivered over a time period is calculated by summing the measured volume flow rates of a time interval, i.e.,

$$V(t_j) = \Delta t \sum_{i=0}^{j} \dot{V}_i \tag{35}$$

where it is assumed that the flow rate measurements are made at regular time intervals Δt. The volume flow rates should be converted to reference conditions [25] before being summed. This conversion is in the form of a multiplication with a correction factor that accounts for the differences in temperature, pressure and compressibility factor between the actual conditions and the reference conditions.

NOTE Equation (35) is an approximation of the integration the continuous function of the mass flow rate over the time interval of interest. This approximation has also an uncertainty, which can be evaluated as described in clause 13.

5.2.2 As far as it concerns the effect of the measurement, the standard uncertainty $V(t_j)$ can be readily obtained using the LPU for correlated input quantities [6, eqn. (13)], or, alternatively, the LPU for multivariate measurement models from ISO/IEC Guide 98-3/Supplement 2:2011 [8].

5.2.3 Using the LPU for correlated input quantities, the expression for the squared standard uncertainty associated with the mass $m(t_j)$ is given by

$$u^2(V(t_j)) = (\Delta t)^2 \sum_{i=0}^{j} u^2(\dot{V}_i) + 2(\Delta t)^2 \sum_{i=0}^{j} \sum_{k=i+1}^{j} u(\dot{V}_i, \dot{V}_k) \tag{36}$$

or, using correlation coefficients,

$$u^2(V(t_j)) = (\Delta t)^2 \sum_{i=0}^{j} u^2(\dot{V}_i) + 2(\Delta t)^2 \sum_{i=0}^{j} \sum_{k=i+1}^{j} r(\dot{V}_i, \dot{V}_k) u(\dot{V}_i) u(\dot{V}_k) \tag{37}$$

NOTE Guidance on how to evaluate the standard uncertainties associated with the flow rates and the correlation coefficients is given in clause 10 of this guide.

5.3 Energy

5.3.1 Depending on whether the mass flow rate or volume flow rate, there are two relationships for calculating the energy over a time interval. Using mass, the relationship reads as

$$E(t_j) = \Delta t \sum_{i=0}^{j} \dot{m}_i \bar{H}_i \tag{38}$$

where $\bar{H}_i$ denotes the calorific value on a mass basis. This calorific value can be obtained from the calorific value on a molar basis and the molar mass of the gas metered [4].

5.3.2 Applying the LPU for dependent input quantities [6, eqn. (13)] to equation (38) yields the expression to calculate the variance (squared standard uncertainty) associated with the energy

$$\begin{aligned} u^2(E(t_j)) = {} & (\Delta t)^2 \sum_{i=1}^{j} \bar{H}^2 u^2(\dot{m}) + (\Delta t)^2 \sum_{i=1}^{j} \dot{m}^2 u^2(\bar{H}) \\ & + 2(\Delta t)^2 \sum_{i=1}^{j-1} \sum_{k=i+1}^{j} \bar{H}_i \bar{H}_k r(\dot{m}_i, \dot{m}_k) u(\dot{m}_i) u(\dot{m}_k) \\ & + 2(\Delta t)^2 \sum_{i=1}^{j-1} \sum_{k=i+1}^{j} \dot{m}_i \dot{m}_k r(\bar{H}_i, \bar{H}_k) u(\bar{H}_i) u(\bar{H}_k) \end{aligned}$$

There are no dependencies to be considered between pairs $\dot{m}_i, \bar{H}_k$.

5.3.3 On a volume basis, the energy is calculated as

$$E(t_j) = \Delta t \sum_{i=0}^{j} \dot{V}_i \tilde{H}_i \tag{39}$$

where $\tilde{H}_i$ denotes the calorific value on a volume basis. This calorific value can be obtained from the calorific value on a molar basis and real gas molar volume of the gas metered [4]. This molar volume is a function of the compressibility factor.

5.3.4 The uncertainty of the time intervals, Δt is generally small and can for practical purposes be neglected.

5.3.5 Applying the LPU for dependent input quantities [6, eqn. (13)] to equation (39) yields the expression to calculate the variance (squared standard uncertainty) associated with the energy

$$\begin{aligned} u^2(E(t_j)) = {} & (\Delta t)^2 \sum_{i=1}^{j} \tilde{H}^2 u^2(\dot{V}) + (\Delta t)^2 \sum_{i=1}^{j} \dot{V}^2 u^2(\tilde{H}) \\ & + 2(\Delta t)^2 \sum_{i=1}^{j-1} \sum_{k=i+1}^{j} \tilde{H}_i \tilde{H}_k r(\dot{V}_i, \dot{V}_k) u(\dot{V}_i) u(\dot{V}_k) \\ & + 2(\Delta t)^2 \sum_{i=1}^{j-1} \sum_{k=i+1}^{j} \dot{V}_i \dot{V}_k r(\tilde{H}_i, \tilde{H}_k) u(\tilde{H}_i) u(\tilde{H}_k) \\ & + (\Delta t) \sum_{i=1}^{j} \sum_{k=1}^{j} \tilde{H}_i \dot{V}_k r(\tilde{H}_i, \dot{V}_k) u(\tilde{H}_i) u(\dot{V}_k) \end{aligned}$$

The correlation coefficients $r(\tilde{H}_i, \dot{V}_k)$ are nonzero due to the volume conversion. Often, both the calorific value and the compressibility factor are computed from the same composition, hence they are correlated. If the calorific value or the compressibility factor are measured independently, then the ultimate covariance terms are zero.

6 Temperature measurement

6.1 Temperature is, along with the pressure, one of the key auxiliary parameters measured in the fiscal metering of gas. It is usually measured using a calibrated temperature transmitter [26].

6.2 Temperature is usually measured in a gas metering station using a transmitter mounted near a flow meter. The temperature thus measured is used for various purposes, e.g.,

- conversion of the gas volume from actual to base conditions [11, 25];
- calculation of the compressibility factor under actual conditions [15, 27–29];
- conversion of other properties to base conditions.

6.3 The measurement model takes into consideration various factors that influence the measurement of the gas temperature. The measurement model takes the form (after [26])

$$T_{\text{gas}} = T_{\text{ind}} + \delta T_{\text{cal}} + \delta T_{\text{RFI}} + \delta T_{\text{drift}} + \delta T_{\text{temp}} + \delta T_{\text{stab}} + \delta T_{\text{other}} \tag{40}$$

where

T_{ind}	temperature indication
δT_{cal}	calibration uncertainty
δT_{RFI}	effect of radio frequency interference
δT_{drift}	drift of the transmitter since it was calibrated
δT_{temp}	temperature effect
δT_{stab}	stability of the temperature element
δT_{other}	other effects

The listed effects are considered to be mutually independent.

6.4 The measurement model (equation (40) does not account for the precision of the measurements, installation effects, temperature difference between the location of the transmitter and the location where the temperature is needed (e.g., the flow meter). These effects can be added by further developing the term δT_{other}.

6.5 Considering the shape of the measurement function (40), the formula for calculating the variance (i.e., squared standard uncertainty) associated with T_{gas} is given by

$$\begin{aligned} u^2(T_{\text{gas}}) = {} & u^2(T_{\text{ind}}) + u^2(\delta T_{\text{cal}}) + u^2(\delta T_{\text{RFI}}) + u^2(\delta T_{\text{drift}}) \\ & + u^2(\delta T_{\text{temp}}) + u^2(\delta T_{\text{stab}}) + u^2(\delta T_{\text{other}}) \end{aligned} \tag{41}$$

which is obtained by using the LPU for independent quantities [6, eqn. (10)] and the measurement function (40).

In a series of measurements from the same instrument, it is important to note that the results of the temperature will be dependent, as some of the factors included in the measurement function (40) are the same for pairs of measurements. In fact, save the uncertainty associated with the indication, all other sources of uncertainty can be considered dependent for two subsequent temperature measurements. In that case, the covariance is given by

$$\begin{aligned} u(T_{\text{gas},i}, T_{\text{gas},j}) = {} & u^2(T_{\text{ind}}) + u^2(\delta T_{\text{cal}}) + u^2(\delta T_{\text{RFI}}) + u^2(\delta T_{\text{drift}}) \\ & + u^2(\delta T_{\text{temp}}) + u^2(\delta T_{\text{stab}}) + u^2(\delta T_{\text{other}}) \qquad (i \neq j) \end{aligned} \tag{42}$$

using equation (F.2) of the GUM [6, Annex F.1].

NOTE An example with representative values and standard uncertainties is given in [30]. It is shown how equation (28) is used for the drift and ambient temperature effects, which are dependent on time and the ambient temperature, respectively.

6.6 The measurement model in equation (40) does not account for the performance of the temperature transmitter when installed in the grid. Such effects include the precision under actual conditions, the mismatch between the temperature of the gas at the transmitter and at the point of interest (e.g., the flow meter), among other effects. A measurement model that includes such effects (δT_{grid}) can be formulated as

$$T_{\text{gas},i} = T_{\text{ind}} + \delta T_{\text{grid},i} + \delta T_{\text{cal}} + \delta T_{\text{RFI}} + \delta T_{\text{drift}} + \delta T_{\text{temp}} + \delta T_{\text{stab}} + \delta T_{\text{other}} \tag{43}$$

The effect $\delta T_{\text{grid},i}$ should be evaluated using time series analysis (see clause 11) to assess dependencies between the measurements arising from effects in the grid.

NOTE Any autocorrelation in the temperature measurements add to the dependence between pairs of measurements. Another source of dependence is the fact that the same measuring instrument is used. The correlations arising from the instrumentation apply to the entire series of measurement results evaluated, whereas the autocorrelation effects are in time much more localised to a one or a few previous measurements (see clause 11).

6.7 If, instead of a detailed analysis of the correlation coefficients between pairs of temperature measurements, a simpler approach is preferred, then the temperature measurements should be treated as (almost) fully correlated, with a correlation coefficient close to 1.

7 Pressure measurement

7.1 Pressure is, along with the temperature, one of the key auxiliary parameters measured in the fiscal metering of gas. It is usually measured using a calibrated pressure transmitter [26].

7.2 The measurement model takes the form (after [26])

$$p_{\text{gas}} = p_{\text{ind}} + \delta p_{\text{cal}} + \delta p_{\text{stab}} + \delta p_{\text{RFI}} + \delta p_{\text{temp}} + \delta p_{\text{atm}} + \delta p_{\text{vib}} + \delta p_{\text{power}} + \delta p_{\text{misc}} \tag{44}$$

where

p_{ind}	pressure indication
δp_{cal}	calibration uncertainty
δp_{RFI}	effect of radio frequency interference
δp_{stab}	stability of the transmitter since it was calibrated
δp_{temp}	temperature effect
δp_{atm}	atmospheric pressure effect
δp_{vib}	effects of vibrations
δp_{power}	effects due to the power supply
δp_{misc}	other effects, such as installation and mounting effects

The listed effects are considered to be mutually independent.

7.3 Using the LPU for independent input quantities [6, equation (10)], the squared standard uncertainty (variance) associated with p_{gas} can be calculated as

$$\begin{aligned} u^2(p_{\text{gas}}) = {} & u^2(p_{\text{ind}}) + u^2(\delta p_{\text{cal}}) + u^2(\delta p_{\text{stab}}) + u^2(\delta p_{\text{RFI}}) + u^2(\delta p_{\text{temp}}) + u^2(\delta p_{\text{atm}}) \\ & + u^2(\delta p_{\text{vib}}) + u^2(\delta p_{\text{power}}) + u^2(\delta p_{\text{misc}}) \end{aligned} \tag{45}$$

7.4 The covariance between two measurements of the pressure can be computed using equation (F.2) from ISO/IEC Guide 98-3:2008 [6]

$$\begin{aligned} u(p_{\text{gas}i}, p_{\text{gas},j}) = {} & u^2(p_{\text{ind}}) + u^2(\delta p_{\text{cal}}) + u^2(\delta p_{\text{stab}}) + u^2(\delta p_{\text{RFI}}) + u^2(\delta p_{\text{temp}}) + u^2(\delta p_{\text{atm}}) \\ & + u^2(\delta p_{\text{vib}}) + u^2(\delta p_{\text{power}}) + u^2(\delta p_{\text{misc}}) \end{aligned} \tag{46}$$

where $p_{\text{gas}i}$ and $p_{\text{gas},j}$ denote a pair of measurements.

7.5 The measurement model in equation (44) does not account for the performance of the pressure transmitter when installed in the grid. Such effects include the precision under actual conditions, the mismatch between the pressure of the gas at the transmitter and at the point of interest (e.g., the flow meter), among other effects. A measurement model that includes such effects (δp_{grid}) can be formulated as

$$p_{\mathrm{gas},i} = p_{\mathrm{ind}} + \delta p_{\mathrm{grid},i} + \delta p_{\mathrm{cal}} + \delta p_{\mathrm{stab}} + \delta p_{\mathrm{RFI}} + \delta p_{\mathrm{temp}} + \delta p_{\mathrm{atm}} + \delta p_{\mathrm{vib}} + \delta p_{\mathrm{power}} + \delta p_{\mathrm{misc}} \quad (47)$$

The effect $\delta p_{\mathrm{grid},i}$ should be evaluated using time series analysis (see clause 11) to assess dependencies between the measurements arising from effects in the grid.

NOTE 1 Any autocorrelation in the pressure measurements add to the dependence between pairs of measurements. Another source of dependence is the fact that the same measuring instrument is used. The correlations arising from the instrumentation apply to the entire series of measurement results evaluated, whereas the autocorrelation effects are in time much more localised to a one or a few previous measurements (see clause 11).

NOTE 2 The treatment of temperature and pressure measurements can be kept very similar. The evaluation of the covariance due to instrumentation (equation (46)) is very similar to that for evaluating the standard uncertainty due to instrumentation (equation (45)).

NOTE 3 The only aspect that can be unrealistic about equation (45) is that the covariance does not depend on the distance between the two pressure measurements. A more sophisticated modelling of the measurement would be required to

7.6 If, instead of a detailed analysis of the correlation coefficients between pairs of pressure measurements, a simpler approach is preferred, then the pressure measurements should be treated as (almost) fully correlated, with a correlation coefficient close to 1 (e.g., 0.99).

8 Composition measurement

8.1 General

8.1.1 Composition measurement is generally done using a gas chromatograph (GC) equipped with an thermal conductivity detector (TCD). The basis for the guidance are the methods in ISO 6974 [2, 3].

8.1.2 Calibration gas mixtures used for composition and energy measurement should be accompanied by a certificate according to ISO 6141 [31]. It should state the amount fractions of the components, their associated expanded uncertainties, the coverage factor(s) and a statement of metrological traceability [16]. For energy measurement, the components covered in the calibration gas mixture shall cover all components found in the gas to be analysed down to an amount fraction of 50 $\mu\mathrm{mol\,mol^{-1}}$ [4]. For calculating the compressibility factor or density, small amount fractions of heavy hydrocarbons can be important to obtain reliable result.

NOTE 1 Metrological traceability aspects of calibration gas mixtures are described in ISO 14167 [32].

NOTE 2 Guidance on metrological traceability in natural gas analysis is given in ISO 14111 [33].

8.1.3 The uncertainty associated with the certified amount fractions of the calibration gas mixture should be taken into account in the choice of regression (if a multipoint calibration approach is used) [2]. Regression methods that ignore the uncertainty in the amount fractions, such as ordinary least-squares regression (OLS) or weighted least-squares regression (WLS) shall not be used to avoid underrating the uncertainty in fiscal metering. ISO 6974 [2, 3] and ISO 6143 [34] describe acceptable regression methods in support of multipoint calibration based on weighted total least-squares regression (WTLS).

8.2 Single point calibration

8.2.1 The measurement described is the analysis of the natural gas composition using an online GC with a single channel and a TCD as detector. The example shows the processing of the data of two natural gas samples, which are processed using the same calibration. Usually these GCs are calibrated once a day.

8.2.2 Let us consider the single point calibration [2, 35] of a natural gas analyser first. The amount fraction x_j of sample j is given by

$$x_j = \frac{A_j}{A_{\mathrm{WS}}} x_{\mathrm{WS}} \tag{48}$$

where x_{WS} denotes the amount fraction of the same component in the working standard, a calibration gas mixture. A_{WS} denotes the response from the working standard (calibration gas mixture [32, 36]). In this scenario, it is assumed that the natural gas analyser is operated with a single calibration. Using the relationship [6, clause 5.1.6]

$$\left[\frac{u(y)}{y}\right]^2 = \sum_{i=1}^{N} \left[\frac{p_i u(x_i)}{x_i}\right]^2 \tag{49}$$

for a multiplicative measurement model of the form $Y = cX_1^{p_1} X_2^{p_2} \ldots X_N^{p_N}$, where the p_i denote the exponents, X_j the input quantities and Y the output quantity of the measurement model, it follows that the sensitivity coefficients in equation (48) are

$$c_{A_j} = \frac{x_j}{A_j}; c_{A_{\mathrm{WS},j}} = -\frac{x_j}{A_{\mathrm{WS}}}; c_{x_{\mathrm{WS},j}} = \frac{x_j}{x_{\mathrm{WS}}} \tag{50}$$

Note that all sensitivity coefficients are a function of the index j.

The covariance between any pair of amount fractions obtained with the same calibrations is given by

$$\begin{aligned} u(x_j, x_k) &= c_{A_{\mathrm{WS},j}} c_{A_{\mathrm{WS},k}} u^2(A_{\mathrm{WS}}) + c_{x_{\mathrm{WS},j}} c_{x_{\mathrm{WS},k}} u^2(x_{\mathrm{WS}}) \\ &= x_j x_k \left(u_{\mathrm{rel}}^2(A_{\mathrm{WS}}) + u_{\mathrm{rel}}^2(x_{\mathrm{WS}})\right) \end{aligned} \tag{51}$$

EXAMPLE Equation (51) makes calculating covariance of this kind of models very straightforward. Let us assume that for the amount fraction carbon dioxide in the WS the relative standard uncertainty is 0.20 %

and the amount fraction $4.0325\,\mathrm{cmol\,mol^{-1}}$, and the repeatability standard deviation of the analyser is $0.10\,\%$. Let $A_{\mathrm{WS}} = 4212\,\mathrm{mV}$, $A_j = 4315\,\mathrm{mV}$ and $A_k = 4344\,\mathrm{mV}$. Now,

$$x_j = \frac{4315}{4212} 4.0325\,\mathrm{cmol\,mol^{-1}} = 4.1311\,\mathrm{cmol\,mol^{-1}}$$

$$x_k = \frac{4344}{4212} 4.0325\,\mathrm{cmol\,mol^{-1}} = 4.2606\,\mathrm{cmol\,mol^{-1}}$$

$$u_{\mathrm{rel}}(x_j) = x_{\mathrm{rel}}(x_k) = \sqrt{(0.20\,\%)^2 + (0.10\,\%)^2 + (0.10\,\%)^2} = 0.24\,\%$$

The covariance is calculated as

$$u(x_j, x_k) = x_j x_k \left[u^2_{\mathrm{rel}}(A_{\mathrm{WS}}) + u^2_{\mathrm{rel}}(x_{\mathrm{WS}})\right] = 8.80 \times 10^{-5}\,\mathrm{cmol^2\,mol^{-2}}$$

and finally the correlation coefficient is computed from [6, equation (14)]

$$r(x_j, x_k) = \frac{u(x_j, x_k)}{u(x_j)u(x_k)} = \frac{8.80 \times 10^{-5}}{0.0101 \cdot 0.0104} = 0.83$$

This calculation shows that there exists a substantial correlation between pairs of amount fractions obtained with the same calibration. The large value for the correlation coefficient stems from the calibration of the instrument in this simple example.

Table 1 shows the composition of a working standard (calibration gas mixture) for the analysis of natural gas up to n-hexane. For the amount fractions of the butanes and neo-pentane, the relative expanded uncertainty is 1.0 % and for the amount fraction methane it is 0.10 %. For the amount fractions of the other components, the expanded uncertainty is 0.50 %. A coverage factor $k = 2$ is used to convert these expanded uncertainties into standard uncertainties.

Table 1: Composition of the calibration gas mixture, expressed in amount fractions ($\mathrm{cmol\,mol^{-1}}$)

Component	x	$U(x)$	$U_{\mathrm{rel}}(x)$
nitrogen	4.090	0.020	0.50
carbon dioxide	1.500	0.008	0.50
methane	88.779	0.089	0.10
ethane	4.000	0.020	0.50
propane	1.000	0.005	0.50
i-butane	0.2000	0.0020	1.00
n-butane	0.2010	0.0020	1.00
neo-pentane	0.0500	0.0005	1.00
i-pentane	0.049 90	0.000 25	0.50
n-pentane	0.049 80	0.000 25	0.50
n-hexane	0.049 90	0.000 25	0.50

Table 2 shows the results of the analysis of two natural gas samples and the calibration of the natural gas analyser. The relative repeatability standard uncertainties shown are obtained from a performance evaluation of the instrument.

The response factors f shown in table 2 are the ratio $A_{\mathrm{WS}}/x_{\mathrm{WS}}$ (see also equation (48)). The response factor for any given component is constant until the next calibration of the analyser with the working standard. So, the correlation between the two composition arises from the response factors.

The raw (non-normalised) compositions, their associated standard uncertainties and correlation coefficients are shown in table 3. The outputs are obtained as follows:

Table 2: Peak areas (A, mV), response factor (f, mV mol cmol^{-1}), repeatability standard deviation (s, mV) and relative repeatability standard deviation (s_{rel}, %) of two natural gas samples

Component	A_1	A_2	f	s	s_{rel}
nitrogen	303 018.6	303 504.6	23 249	244.2	0.08
carbon dioxide	38 691.9	38 733.6	28 277	28.4	0.07
methane	1 585 895.5	1 586 184.1	19 721	1209.9	0.08
ethane	93 465.5	93 595.9	30 690	75.7	0.08
propane	20 218.6	20 190.1	50 144	12.3	0.06
i-butane	5625.1	5613.3	57 946	4.1	0.07
n-butane	5702.6	5714.5	60 120	8.9	0.16
neo-pentane	3064.6	3044.3	58 326	8.0	0.26
i-pentane	3288.9	3286.0	66 778	1.8	0.06
n-pentane	3411.4	3407.2	68 986	2.2	0.07
n-hexane	3831.0	3824.3	77 290	2.7	0.07

Table 3: Raw amount fractions (x_i, cmol mol^{-1}), standard uncertainty associated with the response factor ($u(f)$, mV mol cmol^{-1}), relative standard uncertainty of the response factor ($u_{\text{rel}}(f)$, %), relative standard uncertainty of the amount fractions ($u_{\text{rel}}(f)$, %), covariance between the amount fractions ($u(x_1, x_2)$, cmol^2 mol^{-2}), correlation coefficient between the amount fractions ($r(x_1, x_2)$)

Component	x_1	x_2	$u(f)$	$u_{\text{rel}}(f)$	$u_{\text{rel}}(x)$	$u(x_1, x_2)$	$r(x_1, x_2)$
nitrogen	13.03	13.05	61	0.26	0.27	1.174×10^{-3}	0.91
carbon dioxide	1.368	1.370	74	0.26	0.27	1.272×10^{-5}	0.93
methane	80.42	80.43	18	0.09	0.12	5.380×10^{-3}	0.59
ethane	3.045	3.050	81	0.26	0.27	6.412×10^{-5}	0.91
propane	0.403	0.403	129	0.26	0.26	1.075×10^{-6}	0.95
i-butane	0.0971	0.0969	293	0.51	0.51	2.402×10^{-7}	0.98
n-butane	0.0949	0.0951	315	0.52	0.55	2.474×10^{-7}	0.92
neo-pentane	0.0525	0.0522	329	0.56	0.62	8.735×10^{-8}	0.82
i-pentane	0.049 25	0.049 21	171	0.26	0.26	1.591×10^{-8}	0.95
n-pentane	0.049 45	0.049 39	178	0.26	0.27	1.630×10^{-8}	0.94
n-hexane	0.049 57	0.049 48	201	0.26	0.27	1.655×10^{-8}	0.93

- The amount fractions are obtained using equation (48), or, with the response factor f as $x_i = A_i f^{-1}$.
- The relative standard uncertainty associated with the response factor $u_{\mathrm{rel}}(f)$ is obtained as $\sqrt{u^2_{\mathrm{rel}}(x_{\mathrm{WS}}) + u^2_{\mathrm{rel}}(A_{\mathrm{WS}})}$; the standard uncertainty itself is obtained as $u_{\mathrm{rel}}(f) \cdot f$.
- The relative standard uncertainty associated with the amount fractions is obtained as $\sqrt{u^2_{\mathrm{rel}}(f) + u^2_{\mathrm{rel}}(A_i)}$.
- The covariance between the amount fractions is obtained as $x_1 x_2 u^2_{\mathrm{rel}}(f)$ (see also equation (51)).
- The correlation coefficient can be computed as $u^2_{\mathrm{rel}}(f)/u^2_{\mathrm{rel}}(x)$.

In all symbols, the index for the component was omitted.

8.3 Multipoint calibration

8.3.1 Multipoint calibration is described in ISO 6974 [2,3] and ISO 6143 [34]. To propagate duly the measurement uncertainty associated with the amount fractions of the components and the instrument responses, errors-in-variables regression (EIV) regression shall be used. Other forms of regression, such as WLS or OLS do so only partly or not at all. The WTLS described in ISO 6143 and ISO 6974-1 is a specific form of EIV and suited to propagate the uncertainty from the amount fractions and the responses to the outputs of the regression [37], typically the coefficients of the calibration or analysis function or to the amount fraction of the components in a sample by interpolation.

8.3.2 The most convenient way to apply multipoint calibration is to choose a suite of calibration gas mixtures encompassing the ranges for which the GC is to be calibrated. Details about the number of data points and the number of replicates needed to obtain reliable responses are given in ISO 6974-1 and ISO 6143. These standards shall be followed to calibration the GC. The requirements for the calibration gas mixtures are given in clause 8.1.

8.3.3 The normal use of a calibrated GC is to use it for determining the amount fraction of an unknown gas mixture. This value assignment is described in ISO 6143 [34]. The uncertainty evaluation can be performed using the LPU as given in ISO/IEC Guide 98-3/Supplement 2:2011 [8].

8.3.4 Given formulæ for interpolation in ISO 6143 [34] and ISO 6974-1 [2], the sensitivity coefficients can obtained by analytically, that is, by symbolic differentiation . Given the measurement model (for a cubic analysis function)

$$x = b_0 + b_1 A + b_2 A^2 + b_3 A^3 \tag{52}$$

the expressions for the sensitivity coefficients read as follows

$$\frac{\partial x}{\partial y} = b_1 + 2b_2 A + 3b_3 A^2 \tag{53}$$

$$\frac{\partial x}{\partial b_0}=1$$
$$\frac{\partial x}{\partial b_1}=A$$
$$\frac{\partial x}{\partial b_2}=A^2$$
$$\frac{\partial x}{\partial b_3}=A^3$$

NOTE For a generalised linear model of the form

$$x=\sum_{k=1}^{m} b_k\phi_k(A)$$

the partial derivatives with respect to the b_k are the functions $\phi_k(A)$. For a cubic polynomial, these functions are $\phi_k(A)=A^k$.

8.3.5 The combined standard uncertainty associated with x is obtained using

$$u^2(x)=\left(\frac{\partial g}{\partial y}\right)^2 u^2(y)+\sum_{j=0}^{m}\left(\frac{\partial g}{\partial b_j}\right)^2 u^2\left(b_j\right)+2\sum_{i=0}^{m-1}\sum_{j=i+1}^{m}\left(\frac{\partial g}{\partial b_i}\right)\left(\frac{\partial g}{\partial b_j}\right)u\left(b_i,b_j\right) \tag{54}$$

If, instead of the cubic polynomial of (52) a parabola or straight line is used, then the necessary expressions can be obtained by setting b_2 and b_3 to zero (straight line), or setting bs to zero (parabola) in equations (52) and (53). The expressions for the sensitivity coefficients of b_2 and b_3 (straight line), or setting b_3 (parabola) are in these situations not needed.

8.3.6 For subsequent composition measurements, the same interpolations can be used. The covariance matrix $\boldsymbol{V_x}$ can be obtained using the LPU for multivariate measurement models. For each x_i, the measurement equation takes the form (see equation (52))

$$x_i=b_0+b_1A_i+b_2A_i^2+b_3A_i^3$$

The covariance matrix of the input quantities can be formed as

$$\boldsymbol{V}=\begin{bmatrix}\boldsymbol{V_A} & \boldsymbol{0}\\ \boldsymbol{0} & \boldsymbol{V_b}\end{bmatrix}$$

where $\boldsymbol{V_b}$ denotes the covariance matrix associated with the coefficients $\boldsymbol{b}$ as obtained from regression. The covariance matrix $\boldsymbol{V_A}$ is diagonal, viz.,

$$\boldsymbol{V_A}=\mathrm{diag}\{u^2(A_1),\ldots,u^2(A_N)\}$$

where N denotes the number of compositions measured. The sensitivity matrix $\boldsymbol{C}$ then takes the form

$$\boldsymbol{C}=\begin{bmatrix}\frac{\partial x_1}{\partial A_1} & 0 & 1 & A_1 & A_1^2 & A_1^3\\ 0 & \frac{\partial x_2}{\partial A_2} & 1 & A_2 & A_2^2 & A_2^3\end{bmatrix}$$

for two measurements and a cubic polynomial. The covariance matrix $\boldsymbol{V_x}$ associated with the amount fractions $\boldsymbol{x}$ is then obtained from the matrix product

$$\boldsymbol{V_x} = \boldsymbol{C}\boldsymbol{V}\boldsymbol{C}^\top$$

Note that in this clause, $\boldsymbol{x}$ is a vector holding the amount fractions of a single component and that $\boldsymbol{V_x}$ is the associated covariance matrix.

NOTE $\boldsymbol{x}$ and $\boldsymbol{V_x}$ are not to be confused with the composition vector introduced in clause 8.4

8.4 Normalisation

8.4.1 The calculation of natural gas properties is fundamental to the trade in natural gas. Many contracts in this area are energy-based, which means that the energy content (calorific value) of the gas transmitted plays as important a role as the volume or mass of natural gas [11, 13, 38].

8.4.2 For use in calculations, the natural gas composition should meet the requirement of any composition, namely that the sum of all fractions forming it is exactly equal to a constant [39]. This condition can be expressed as

$$\sum_{j=1}^{n} x_j = \kappa \tag{55}$$

where x_j denote the normalised amount fractions of the components j, and n the number of components. κ is the normalisation constant. When expressing amount fractions in $\mathrm{mol\,mol^{-1}}$, $\kappa = 1\,\mathrm{mol\,mol^{-1}}$, whereas when expressing these in $\mathrm{cmol\,mol^{-1}}$, $\kappa = 100\,\mathrm{cmol\,mol^{-1}}$, and so on [39].

8.4.3 A composition calculated from (gravimetric) gas mixture preparation [40, 41] always meets the normalisation constraint (equation (55)), as it is inherent to the measurement equation used. Not all measurement procedures provide amount fractions that sum exactly to the normalisation constant. When using compositional data from, e.g., a gas chromatographic determination, the constraint shall be enforced by normalising the amount fractions. Amount fractions that do not meet the mathematical constraint of a composition are sometimes called “raw” amount fractions to distinguish them from (normalised) amount fractions that satisfy the condition.

8.4.4 Ensuring that a composition expressed in amount fraction satisfies this condition can be achieved by using, e.g., the normalisation procedure from ISO 6974 [2, 3], also known as *closure* of a composition [39]. The normalisation procedure is described in ISO 6974-1 [2] and the uncertainty calculation is given in ISO 6974-2 [3]. These procedures shall be used to process non-normalised compositions.

8.4.5 The normalised amount fraction x_i is related to the raw amount fraction $\tilde{x}_i$ as follows [2,3]

$$x_i = \frac{\kappa \tilde{x}_i}{\sum_{j=1}^{n} \tilde{x}_j} \tag{56}$$

The covariance matrix associated with the vector of the normalised amount fractions $\boldsymbol{x}$, $\boldsymbol{V}_{\boldsymbol{x}}$, can be calculated from the covariance matrix $\boldsymbol{V}_{\tilde{\boldsymbol{x}}}$ associated with the raw amount fractions as follows [8]

$$\boldsymbol{V}_{\boldsymbol{x}} = \boldsymbol{C}\boldsymbol{V}_{\tilde{\boldsymbol{x}}}\boldsymbol{C}^{\top} \tag{57}$$

where the elements of the sensitivity matrix $\boldsymbol{C}$ are given by

$$C_{ii} = \frac{\kappa}{\Xi} - \frac{\kappa \tilde{x}_i}{\Xi^2} \tag{58}$$

$$C_{ij} = -\frac{\kappa \tilde{x}_i}{\Xi^2} \qquad (i \neq j) \tag{59}$$

and $\Xi = \sum_{j=1}^{n} \tilde{x}_j$.

8.4.6 The covariance matrix of a normalised composition has some special features. In each row (and column) the elements of $\boldsymbol{V}_{\boldsymbol{x}}$ add to zero, which is a property of the uncertainty of a composition [39]. Equation (60) is a convenient way to verify whether the covariance matrix of a composition is valid for use in uncertainty calculations [39]. In matrix form, this check can be performed by verifying whether

$$\boldsymbol{1}^{\top}\boldsymbol{V}_{\boldsymbol{x}}\boldsymbol{1} = 0 \tag{60}$$

where **1** denotes a column vector of length n, whose elements are all 1. Equation (60) is a direct consequence of the condition given in equation (55).

8.4.7 Compositions meeting the normalisation constraint (55) have a covariance matrix that is singular. Depending on how a composition is formed [42], the covariance matrix looks different. Considering that – at least in principle – both the input compositions and the output compositions have associated covariance matrices, the LPU for multivariate measurement models from ISO/IEC Guide 98-3/Supplement 2:2011 [8] is used.

8.4.8 For a single non-normalised composition $\tilde{\boldsymbol{x}}_1$ with associated covariance matrix $\boldsymbol{V}_{\tilde{\boldsymbol{x}}_1}$, the covariance matrix associated with the normalised composition $\boldsymbol{x}_1$ is given by

$$\boldsymbol{V}_{\boldsymbol{x}_1} = \boldsymbol{C}_1\boldsymbol{V}_{\tilde{\boldsymbol{x}}_1}\boldsymbol{C}_1^{\top} \tag{61}$$

where the elements of the sensitivity matrix $\boldsymbol{C}_1$ are given by

$$C_{ii,1} = \frac{\kappa}{\Xi_1} - \frac{\kappa x_{i,1}}{\Xi_1^2} \tag{62}$$

$$C_{ij,1} = -\frac{\kappa x_{i,1}}{\Xi_1^2} \qquad (i \neq j) \tag{63}$$

and $\Xi_1 = \sum_{k=1}^{n} \tilde{x}_{k,1}$. The normalised amount fractions are given by $x_{i,1} = \tilde{x}_{i,1}\Xi_1^{-1}$ [2].

8.4.9 Consider now two compositions that are correlated due to the fact that they have been measured with the same gas chromatograph with the same calibration. Let the sensitivity matrix for composition $\tilde{\boldsymbol{x}}_i$ be noted by $\boldsymbol{C}_1$ and that for composition $\tilde{\boldsymbol{x}}_2$ by $\boldsymbol{C}_2$. For both compositions, equations (62) and (63) provide the expressions to form them.

8.4.10 Let us consider the case typical for subsequent composition measurements, where a series of correlation coefficients is available, for each pair of amount fractions of a component one. The correlation matrix associated with the two compositions given by

$$\tilde{\boldsymbol{R}}_{12} = \begin{bmatrix} \boldsymbol{I} & \tilde{\boldsymbol{R}} \\ \tilde{\boldsymbol{R}} & \boldsymbol{I} \end{bmatrix} \tag{64}$$

where $\boldsymbol{I}$ denotes an $n \times n$ identity matrix and $\boldsymbol{R}$ the correlation matrix between the two compositions

$$\tilde{\boldsymbol{R}} = \mathrm{diag}\{\tilde{r}_1, \ldots, \tilde{r}_n\}$$

where $\tilde{r}_i$ is shorthand for the correlation coefficient $r(\tilde{x}_1, \tilde{x}_2)$. To obtain the covariance matrix $\tilde{\boldsymbol{V}}_{12}$, a diagonal matrix is needed with the standard uncertainties associated with the raw amount fractions, viz.,

$$\tilde{\boldsymbol{D}}_{12} = \mathrm{diag}\{u(\tilde{x}_{11}), \ldots, u(\tilde{x}_{1n}), u(\tilde{x}_{12}), \ldots, u(\tilde{x}_{2n}))$$

where the $u(\tilde{x}_{ij})$ denotes the standard uncertainty associated with the non-normalised amount fraction $\tilde{x}_i$ in composition j. The covariance matrix $\tilde{\boldsymbol{V}}_{12}$ associated with the two non-normalised compositions is calculated as

$$\tilde{\boldsymbol{V}}_{12} = \tilde{\boldsymbol{D}}_{12} \tilde{\boldsymbol{R}}_{12} \tilde{\boldsymbol{D}}_{12}$$

The covariance matrix $\boldsymbol{V}_{\mathbf{12}}$ associated with the normalised compositions $\boldsymbol{x}_{\mathbf{1}}$ and $\boldsymbol{x}_{\mathbf{2}}$ is given by

$$\boldsymbol{V}_{\boldsymbol{x}_{12}} = \boldsymbol{C}_{\mathbf{12}} \boldsymbol{V}_{\tilde{\boldsymbol{x}}_{12}} \boldsymbol{C}_{\mathbf{12}}^{\top} \tag{65}$$

where

$$\boldsymbol{C}_{\mathbf{12}} = \begin{bmatrix} \boldsymbol{C}_{\mathbf{1}} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{C}_{\mathbf{2}} \end{bmatrix} \tag{66}$$

where $\boldsymbol{C}_{\mathbf{1}}$ and $\boldsymbol{C}_{\mathbf{2}}$ are calculated using equations (62) and (63).

EXAMPLE Using the non-normalised composition from table 3, the normalised compositions are given in table 4.

The sub matrices of the correlation matrix are given in tables 5, 6 and 7. The correlation matrix is given by

$$\boldsymbol{R} = \begin{bmatrix} \boldsymbol{R}_1 & \boldsymbol{R}_{12} \\ \boldsymbol{R}_{12} & \boldsymbol{R}_2 \end{bmatrix} \tag{67}$$

The covariance matrix associated with the vector holding the two compositions can be computed using [7]

$$\boldsymbol{V} = \boldsymbol{DRD}$$

where

$$\boldsymbol{D}^{\top} = \mathrm{diag}\{u(x_{11}), \ldots, u(x_{N1}), u(x_{12}), \ldots, u(x_{N2})\}$$

Table 4: Normalised amount fractions (x_i, cmol mol^{-1}), relative standard uncertainty associated with the amount fractions ($u_{\mathrm{rel}}(x)$, %), correlation coefficient between the amount fractions ($r(x_1, x_2)$)

Component	x_1	x_2	$u_{\mathrm{rel}}(x)$	$r(x_1, x_2)$
Nitrogen	13.21	13.23	0.26	0.87
Carbon dioxide	1.387	1.3878	0.29	0.89
Methane	81.51	81.49	0.04	0.83
Ethane	3.087	3.0898	0.29	0.88
Propane	0.409	0.4079	0.28	0.90
i-Butane	0.0984	0.0981	0.52	0.97
n-Butane	0.0961	0.0963	0.56	0.91
neo-Pentane	0.0533	0.0529	0.63	0.82
i-Pentane	0.049 92	0.049 85	0.28	0.91
n-Pentane	0.050 12	0.050 04	0.29	0.90
n-Hexane	0.050 24	0.050 13	0.29	0.89

Table 5: Correlation matrix $\boldsymbol{R}_1$ associated with the first normalised composition. The order of the components is the same as in table 4.

1	-0.003	-0.956	-0.020	0.007	0.004	0.004	0.004	0.011	0.011	0.011
-0.003	1	-0.140	0.091	0.117	0.064	0.060	0.053	0.121	0.119	0.118
-0.956	-0.140	1	-0.246	-0.082	-0.043	-0.042	-0.034	-0.062	-0.061	-0.061
-0.020	0.091	-0.246	1	0.101	0.055	0.051	0.046	0.105	0.103	0.102
0.007	0.117	-0.082	0.101	1	0.070	0.065	0.058	0.131	0.129	0.128
0.004	0.064	-0.043	0.055	0.070	1	0.035	0.031	0.072	0.071	0.070
0.004	0.060	-0.042	0.051	0.065	0.035	1	0.029	0.067	0.066	0.065
0.004	0.053	-0.034	0.046	0.058	0.031	0.029	1	0.059	0.059	0.058
0.011	0.121	-0.062	0.105	0.131	0.072	0.067	0.059	1	0.133	0.132
0.011	0.119	-0.061	0.103	0.129	0.071	0.066	0.059	0.133	1	0.130
0.011	0.118	-0.061	0.102	0.128	0.070	0.065	0.058	0.132	0.130	1

Table 6: Correlation matrix $\boldsymbol{R}_2$ associated with the second normalised composition. The order of the components is the same as in table 4.

1	-0.003	-0.956	-0.021	0.007	0.004	0.004	0.004	0.011	0.011	0.011
-0.003	1	-0.140	0.091	0.117	0.064	0.060	0.053	0.121	0.119	0.118
-0.956	-0.140	1	-0.246	-0.082	-0.043	-0.042	-0.034	-0.062	-0.061	-0.061
-0.021	0.091	-0.246	1	0.101	0.055	0.051	0.046	0.105	0.103	0.102
0.007	0.117	-0.082	0.101	1	0.070	0.065	0.058	0.131	0.129	0.128
0.004	0.064	-0.043	0.055	0.070	1	0.035	0.031	0.072	0.071	0.070
0.004	0.060	-0.042	0.051	0.065	0.035	1	0.029	0.067	0.066	0.065
0.004	0.053	-0.034	0.046	0.058	0.031	0.029	1	0.059	0.059	0.058
0.011	0.121	-0.062	0.105	0.131	0.072	0.067	0.059	1	0.133	0.132
0.011	0.119	-0.061	0.103	0.129	0.071	0.066	0.059	0.133	1	0.130
0.011	0.118	-0.061	0.102	0.128	0.070	0.065	0.058	0.132	0.130	1

Table 7: Correlation sub matrix $\boldsymbol{R}_{12}$ associated with the normalised amount fractions of the components between the two compositions. The order of the components is the same as in table 4.

0.868	-0.044	-0.812	-0.060	-0.035	-0.019	-0.018	-0.015	-0.032	-0.032	-0.031
-0.044	0.888	-0.073	0.046	0.069	0.038	0.035	0.032	0.072	0.071	0.071
-0.812	-0.073	0.831	-0.169	-0.019	-0.010	-0.010	-0.005	0.000	0.000	0.000
-0.060	0.046	-0.169	0.876	0.054	0.030	0.028	0.025	0.058	0.057	0.056
-0.035	0.069	-0.019	0.054	0.904	0.043	0.040	0.036	0.081	0.080	0.080
-0.019	0.038	-0.010	0.030	0.043	0.965	0.022	0.019	0.044	0.044	0.043
-0.018	0.035	-0.010	0.028	0.040	0.022	0.908	0.018	0.042	0.041	0.041
-0.015	0.032	-0.005	0.025	0.036	0.019	0.018	0.818	0.037	0.037	0.036
-0.032	0.072	0.000	0.058	0.082	0.044	0.042	0.037	0.910	0.084	0.083
-0.032	0.071	0.000	0.057	0.080	0.044	0.041	0.037	0.084	0.899	0.082
-0.032	0.071	0.000	0.056	0.080	0.043	0.041	0.036	0.083	0.082	0.892

8.5 Covariance matrix from normalised composition data

8.5.1 In industry, data transfers are usually restricted to reporting the normalised amount fractions of the components. The uncertainty of these amount fractions is usually known to a certain extent, for example from subjecting the natural gas analyser to a performance evaluation as described in ISO 10723 [43] or by evaluating the measurement uncertainty in accordance with ISO 6974-2 [3] and propagating it when performing the normalisation.

8.5.2 Whereas it is recommended to provide measurement results with an uncertainty, and where relevant, also with covariances (or, equivalently, correlation coefficients) [6,8,44], practice is different. Yet, it can be readily shown that in the case of natural gas properties, ignoring the correlations between the amount fractions of the components has a serious impact [21].

8.5.3 In many uncertainty calculations in metrology, it is impossible to recover covariances without having a detailed insight in the underlying uncertainty calculations. In the case of natural gas composition data, there is an agreed method to normalise the data (described in ISO 6974 [2,3]). Under the assumption that the normalisation method of ISO 6974 has been used, it is possible to recover the covariances from the normalised compositions and their associated standard uncertainties alone. The algorithm is presented in section 8.4.

8.5.4 The reconstruction of the covariance matrix is based on the considerations discussed in section 8.4. The expressions for the sensitivity coefficients (see equations (58) and (59)) require the raw sum Ξ and the raw amount fractions $\tilde{x}_i$. These are however unknown when only normalised fractions are at hand, but they can be approximated by $\Xi \approx \kappa$ and $\tilde{x}_i \approx x_i$ for all components i. These approximations are sufficient for the uncertainty calculation, but obviously not to provide values for the raw amount fractions. Only when the raw sum Ξ were known, these raw fractions can be reconstructed as well, and there would be no need to approximate the sensitivity matrix $\boldsymbol{C}$ using equations (69) and (70).

8.5.5 The first step in the recovery algorithm is to calculate the variances (squared standard uncertainties) associated with the raw amount fractions. These are related to the variances of the normalised ones through equation (57). For $u^2(x_k)$ this relationship reads as

$$u^2(x_k) = \sum_{j=1}^{n} C_{kj}^2 u^2(\tilde{x}_j) \quad k = 1, \ldots, n. \tag{68}$$

The sensitivity coefficients can be approximated by

$$C'_{ii} \approx 1 - \frac{x_i}{\kappa} \tag{69}$$

$$C'_{ij} \approx -\frac{x_i}{\kappa} \qquad (i \neq j) \tag{70}$$

which follows from equations (58) and (59), respectively, by considering that $x_i \approx \tilde{x}_i$ for all i and $\Xi \approx \kappa$. Substituting equations (69) and (70) into the n equations (68) leads to a set of n linear equations where the $u^2(\tilde{x}_j)$ are the unknowns. This set can be represented as

$$\boldsymbol{A}\boldsymbol{v}_{\tilde{\boldsymbol{x}}} = \boldsymbol{v}_{\boldsymbol{x}} \tag{71}$$

where $\boldsymbol{v}_{\boldsymbol{x}} = \left(u^2(x_1), \ldots u^2(x_n)\right)^\top$, and $\boldsymbol{v}_{\tilde{\boldsymbol{x}}} = \left(u^2(\tilde{x}_1), \ldots u^2(\tilde{x}_n)\right)^\top$. The elements of the matrix $\boldsymbol{A}$ are $A_{ij} = {C'_{ij}}^2$, where C' is given by equations (69) and (70).

8.5.6 The solution of equation (71) is given by $\boldsymbol{v}_{\tilde{\boldsymbol{x}}} = \boldsymbol{A}^{-1}\boldsymbol{v}_{\boldsymbol{x}}$, but directly inverting the matrix $\boldsymbol{A}$ is not the best way of solving a set of linear equations. The set can better be solved using a stable numerical method, such as QR-factorisation or singular value decomposition [21, 45].

8.5.7 Using QR-factorisation for example, compute first the factorisation

$$\boldsymbol{A} = \boldsymbol{Q}\boldsymbol{R}$$

where $\boldsymbol{Q}$ is an orthogonal matrix and $\boldsymbol{R}$ an upper triangular matrix. Then, compute

$$\boldsymbol{v}'_{\boldsymbol{x}} = \boldsymbol{Q}^\top \boldsymbol{v}_{\boldsymbol{x}}$$

and then solving

$$\boldsymbol{R}\boldsymbol{v}_{\tilde{\boldsymbol{x}}} = \boldsymbol{v}'_{\boldsymbol{x}} \tag{72}$$

by back substitution [46, section 2.4]. In `R` [47], the solution of the set of linear equations (71) can be obtained by a call to the function `qr.solve()` [21].

NOTE QR factorisation is not available in mainstream spreadsheet software. Whereas generally orthogonal factorisation of the matrix $\boldsymbol{A}$ is the preferred method to minimise loss of accuracy, other ways of solving a linear set of equations can be used instead.

Once the vector $\boldsymbol{v}_{\tilde{\boldsymbol{x}}}$ is obtained, it can be converted to (an approximation of) the diagonal covariance matrix $\boldsymbol{V}_{\tilde{\boldsymbol{x}}}$ and used in equation (57) to obtain the full covariance matrix $\boldsymbol{V}_{\boldsymbol{x}}$.

EXAMPLE The recovery algorithm for the covariance matrix of the composition (see section 8.5) has been implemented in R [47]. The default solver for a set of linear equations is using the QR-factorisation. Consider the simple raw composition in table 8. The standard uncertainties in this example are neither intended to represent typical performance let alone state-of-the-art natural gas measurement results. The increase of the relative standard uncertainties from methane (CH_4) to propane (C_3H_8) as well as those for nitrogen and carbon dioxide represent a typical uncertainty structure for a composition measurement of natural gas. The sum of the amount fractions is $\Xi = 99.034\,\mathrm{cmol\,mol^{-1}}$.

Table 8: Non-normalised composition of a natural gas containing 5 components, expressed in amount fractions ($\mathrm{cmol\,mol^{-1}}$)

Component	x $\mathrm{cmol\,mol^{-1}}$	$u(x)$ $\mathrm{cmol\,mol^{-1}}$	$u_{\mathrm{rel}}(x)$
Nitrogen	3.248	0.021	0.65 %
Carbon dioxide	2.398	0.018	0.75 %
Methane	83.520	0.209	0.25 %
Ethane	6.523	0.044	0.67 %
Propane	3.345	0.113	3.38 %

To illustrate the recovery algorithm, the normalised composition computed from the data in table 8 is used, i.e.,

$$\boldsymbol{x}^{\top} = (3.280, 2.421, 84.335, 6.587, 3.378)$$
$$\boldsymbol{v}_{\boldsymbol{x}}^{\top} = (0.022^2, 0.019^2, 0.211^2, 0.044^2, 0.110^2)$$

Solving the set of linear equations yields

$$\boldsymbol{v}_{\tilde{\boldsymbol{x}}}^{\top} = (0.021^2, 0.018^2, 0.209^2, 0.044^2, 0.113^2)$$

which are the recovered standard uncertainties associated with the raw amount fractions. The relative difference between the standard uncertainties associated with the raw amount fractions thus recovered and the original ones (see table 8) is -0.97 %, which is acceptable for an uncertainty calculation. The covariance matrix $\boldsymbol{V}_{\boldsymbol{x}}$ computed with the recovered values for the standard uncertainties differs negligibly from that computed directly from the data in table 8. The performance of this recovery algorithm depends on the value of the raw sum Ξ. In most practical cases, the raw sum is $98\,\mathrm{cmol\,mol^{-1}} \leq \Xi \leq 102\,\mathrm{cmol\,mol^{-1}}$, which is close enough to $100\,\mathrm{cmol\,mol^{-1}}$ for using this recovery algorithm.

The correlation matrices after normalisation and from recovery are shown in table 9. The values of the correlation coefficients are identical up to four digits, which is more than sufficient for accepting the outcome of the recovery algorithm for an uncertainty evaluation [44, 48].

9 Gas properties

9.1 General

9.1.1 Natural gas properties play a key role in the volumetric metering of gas, as well as in the measurement of energy. The volume flow rate is converted from actual to reference conditions.

Table 9: Correlation matrices of the normalised composition (upper triangle) and from recovery (lower triangle) [21]

Component	N_2	CO_2	CH_4	C_2H_6	C_3H_8
N_2	1	0.0635	−0.0703	0.0367	−0.1543
CO_2	0.0635	1	−0.0605	0.0320	−0.1341
CH_4	−0.0703	−0.0605	1	−0.2531	−0.8782
C_2H_6	0.0367	0.0320	−0.2531	1	−0.1609
C_3H_8	−0.1543	−0.1341	−0.8782	−0.1609	1

This correction factor is given by

$$\frac{\dot{V}_0}{\dot{V}} = \frac{p T_0 Z_0}{p_0 T Z} \tag{73}$$

where $\dot{V}_0$ denotes the volume flow rate at reference conditions, $\dot{V}$ the volume flow rate as measured at temperature T and pressure p. The compressibility factors at actual and reference conditions are denoted by Z and Z_0, respectively, and the reference pressure is denoted by p_0 and the reference pressure by T_0.

9.1.2 In energy measurement, the volumetric calorific value comes into play as well, which also depends on the compressibility factor, albeit not necessarily by the same reference conditions [4, 11].

9.1.3 The propagation of measurement uncertainty from the composition and component properties is described in ISO 6976, Annex B [4]. This treatise is taken as starting point in this guide. The only exception that is made is that this guide deprecates ignoring the correlation coefficients between the amount fractions in the normalised gas composition [4]. Table 10 illustrates why it is generally not appropriate to ignore these correlation coefficients.

Table 10: Calculation of natural gas properties with correlations, using the recovered correlation matrix, and without correlations. Shown are the molar superior calorific value (H, $\mathrm{kJ\,mol^{-1}}$), molar mass ($\bar{M}$, $\mathrm{g\,mol^{-1}}$), compressibility factor (Z), superior calorific value on a mass basis (H_m, $\mathrm{MJ\,kg^{-1}}$), and on volume basis for a real gas ($\tilde{H}$, $\mathrm{MJ\,m^{-3}}$). [21]

	With Correlations		Recovery		Without Correlations	
	x	$u(x)$	x	$u(x)$	x	$u(x)$
H	929.8	1.5	929.8	1.5	929.8	2.7
$\bar{M}$	18.984	0.030	18.984	0.030	18.984	0.055
Z	0.997448	0.000045	0.997448	0.000045	0.997448	0.000048
H_m	48.977	0.030	48.977	0.030	48.977	0.20
$\tilde{H}$	39.423	0.065	39.423	0.065	39.423	0.117

9.1.4 The guidance in this document is not limited to ISO 6976 [4]. Much of what is being provided to work with the natural gas properties in ISO 6976 applies equally to the use of equations of state as described in, e.g., ISO 12213 [27,28] and ISO 20765 [15,29].

9.2 Calculation from composition

One of the most widely used methods to obtain natural gas properties is by calculation from composition. In subsequent calculations involving the quantities obtained, the covariances between the natural gas properties are needed, alongside the standard uncertainties and values for them. ISO 6976 [4, Annex B] provides a consistent propagation and evaluation of the measurement uncertainty associated with the gas properties covered by said standard. The treatise is elaborated to evaluate the covariances between calorific values, compressibility factors and molar masses from subsequent measurements of the composition (see also clause 8.4 and clause 5.3.

9.2.1 From three natural gas properties mentioned in ISO 6976, all other natural properties can be calculated. The base properties are the calorific value on a molar basis, the compressibility factor and the molar mass. Together with the molar mass of air and the compressibility factor of air, all other properties can be calculated.

9.2.2 It is convenient to express the measurement model for calculating the relevant natural gas properties in two stages. In stage 1, the three base properties are calculated and a full covariance matrix obtained. Using these, all other properties can be calculated. Hence, the output vector $\boldsymbol{\xi}$ of the first stage can be defined as

$$\xi = \left[H, \bar{M}, Z\right]^{\top} \tag{74}$$

where H denotes the calorific value on a molar basis, $\bar{M}$ the molar mass of the natural gas and Z the compressibility of the natural gas. For brevity of notation, the combustion temperature t_1 and the metering conditions t_2, p_2 have been omitted. In the first stage of the measurement model, the properties listed in equation (74) are calculated. In a second stage, all or selected natural gas properties can be computed, and the covariance matrix, holding, among others, the squares standard uncertainties of these properties.

9.2.3 The input quantities needed for the first stage are the composition $\boldsymbol{x}$, the pure substance calorific values $\boldsymbol{h}$, the molar masses $\boldsymbol{M}$, and the coefficients needed for computing the compressibility $\boldsymbol{s}$. Thus, the input vector of the first stage can be defined as

$$\zeta_{\mathbf{sup}} = \left[\boldsymbol{H}^{\top}, \boldsymbol{M}^{\top}, \boldsymbol{s}^{\top}, \boldsymbol{y}^{\top}\right]^{\top} \tag{75}$$

9.2.4 As stated previously in the first stage three natural gas properties are calculated, H^0, $\bar{M}$, and Z. The properties of air are included in the calculation of the covariance matrix $\boldsymbol{V}_{\xi_{\mathbf{sup}}}$

associated with the vector $\boldsymbol{\xi}_{\mathbf{sup}}$ holding the output variables of this stage of the measurement model. The calculation is performed as follows

$$\boldsymbol{V}_{\xi_{\text{sup}}} = \boldsymbol{C}_{\zeta} \boldsymbol{V}_{\zeta_{\text{sup}}} \boldsymbol{C}_{\zeta}^{\top} \tag{76}$$

where $\boldsymbol{V}_{\xi}$ denotes the sensitivity matrix and $\boldsymbol{V}_{\zeta_{\text{sup}}}$ the covariance matrix of the input variables, i.e.,

$$\boldsymbol{V}_{\zeta_{\text{sup}}} = \text{diag}\{\boldsymbol{V}_{\boldsymbol{H}}, \boldsymbol{V}_{\boldsymbol{M}}, \boldsymbol{V}_{\boldsymbol{s}}, \boldsymbol{V}_{\boldsymbol{y}}, u^2(M_{\text{air}}), u^2(Z_{\text{air}})\} \tag{77}$$

As ISO 6976 [4] assumes the enthalpies H_j and the coefficients s_j as mutually independent, the corresponding covariance matrices $\boldsymbol{V}_{\boldsymbol{H}}$ and $\boldsymbol{V}_{\boldsymbol{s}}$ are diagonal. On the other hand, the molar masses of the components are usually correlated. The calculation of the covariances is described in ISO 6976 [4]; the calculation of the covariance matrix $\boldsymbol{V}_{\boldsymbol{M}}$ is discussed elsewhere [40]. The calculation of the covariance matrix $\boldsymbol{V}_{\boldsymbol{x}}$ was discussed in section 8.4. The standard considers the compressibility (Z_{air}) and the molar mass (M_{air}) of air as independent of the other properties, and this convention will be used here as well. The values for the standard uncertainties associated with Z_{air} and M_{air} are 0.000 015 and 0.004 respectively for all metering temperatures covered in ISO 6976 [4].

9.2.5 The formation of the sensitivity matrix, the matrix holding the sensitivity coefficients, can be carried out as follows. A convenient way to develop the expressions for the sensitivity coefficient is to write the equations forming the measurement model as total differentials [40]. Any function f with n input variables $x_1, \ldots, x_n$ that is differentiable can be written as total differential [49]

$$\mathrm{d}f = \frac{\partial f}{\partial x_1} \mathrm{d}x_1 + \cdots + \frac{\partial f}{\partial x_n} \mathrm{d}x_n$$

The factors before $\mathrm{d}x_1, \ldots, \mathrm{d}x_n$ are the sensitivity coefficients as they appear in the law of propagation of uncertainty [6,8]. Total differentials also provide a convenient mechanism for applying the chain rule of differentiation [49]. the partial derivatives appearing in a total differential form a row in the sensitivity matrix; the sensitivity coefficients of the variables not present in the total differential are zero.

9.2.6 Writing the expression for the superior calorific value from ISO 6976 [4] on a molar basis as a total differential yields

$$\mathrm{d}H_{\text{sup}} = \sum_{j=1}^{n} H_j \, \mathrm{d}y_j + \sum_{j=1}^{n} y_j \, \mathrm{d}H_j$$

For the molar mass [4], an analogous expression is obtained

$$\mathrm{d}\bar{M} = \sum_{j=1}^{n} M_j \, \mathrm{d}y_j + \sum_{j=1}^{n} y_j \, \mathrm{d}M_j$$

In the same vein, the expression for the compressibility can be developed

$$\mathrm{d}Z = -\frac{p_2}{p_0} 2S\,\mathrm{d}S \tag{78}$$

where $S = \sum_{j=1}^{n} y_j s_j$ and thus

$$\mathrm{d}S = \sum_{j=1}^{n} s_j\,\mathrm{d}y_j + \sum_{j=1}^{n} y_j\,\mathrm{d}s_j \tag{79}$$

p_0 denotes the reference pressure (101 325 Pa) [4] and p_2 the metering pressure. Substitution of equation (79) into (78) is an application of the chain rule of differentiation [49] and yields the expressions for the sensitivity coefficients of Z with respect to the input variables (the y_j and the s_j). The expression for the sensitivity matrix $\boldsymbol{C}_\zeta$ reads as

$$\boldsymbol{C}_\zeta = \begin{bmatrix} \boldsymbol{y}^\top & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{H}^\top \\ \boldsymbol{0} & \boldsymbol{y}^\top & \boldsymbol{0} & \boldsymbol{M}^\top \\ \boldsymbol{0} & \boldsymbol{0} & c\boldsymbol{y}^\top & c\boldsymbol{s}^\top \end{bmatrix} \tag{80}$$

where $c = -\frac{p_2}{p_0} \sum_{j=1}^{n} y_j s_j$.

9.2.7 For calculations on inferior base, a few modifications are needed to the expressions developed for the superior base. In the input vector, the vector $\boldsymbol{H}$ holding the pure component superior calorific values should be replaced by the vector $\boldsymbol{H}'$ holding the pure component inferior calorific values. Also the covariance matrix $\boldsymbol{V}_{\boldsymbol{H}}$ should be replaced by a covariance matrix $\boldsymbol{U}'_{\boldsymbol{H}}$ holding the uncertainty information for the calorific values on an inferior base. The vector $\boldsymbol{H}'$ can be defined as

$$\boldsymbol{H}' = \boldsymbol{H} - \boldsymbol{L}$$

where the elements of the vector $\boldsymbol{L}$ are given by $L_j = \frac{1}{2} b_j L^0(t_1)$. The covariance matrix associated with this vector is given by

$$\boldsymbol{V}_{\boldsymbol{L}} = \boldsymbol{b}\boldsymbol{b}^\top u^2(L^0)$$

where $\boldsymbol{b}$ denotes a vector whose elements are $-\frac{1}{2} b_j$. The covariance matrix $\boldsymbol{H}'$ is given by

$$\boldsymbol{U}'_{\boldsymbol{H}} = \boldsymbol{V}_{\boldsymbol{H}} + \boldsymbol{V}_{\boldsymbol{L}}$$

9.2.8 The vector with input quantities now reads as

$$\boldsymbol{\zeta}^\top_{\mathbf{inf}} = \left(\boldsymbol{H}'^\top, \boldsymbol{M}^\top, \boldsymbol{s}^\top, \boldsymbol{y}^\top, M_{\mathrm{air}}, Z_{\mathrm{air}}\right)$$

With these expressions, the covariance matrix $\boldsymbol{V}_{\xi_{\mathrm{inf}}}$ can be written as follows

$$\boldsymbol{V}_{\xi_{\mathrm{inf}}} = \boldsymbol{C}_\zeta \begin{bmatrix} \boldsymbol{V}'_{\boldsymbol{H}} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{V}_{\boldsymbol{M}} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_{\boldsymbol{s}} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_{\boldsymbol{y}} \end{bmatrix} \boldsymbol{C}_\zeta^\top$$

The sensitivity matrix $\boldsymbol{C}_\zeta$ is given by equation (80), where $\boldsymbol{H}$ should be replaced by $\boldsymbol{H}'$ for the inferior base.

EXAMPLE The Wobbe index of a real gas is defined as quotient of the gross calorific value on a volume basis divided by the square root of the relative density, viz.,

$$W = \frac{H}{V^0 Z \sqrt{d}} \tag{81}$$

where V^0 is the ideal gas volume and d the relative density at reference metering conditions (t_1, p_1). Writing equation 81 provides the expressions for the sensitivity coefficients

$$\begin{aligned}
\mathrm{d}W = {} & \frac{1}{V^0 Z \sqrt{d}} \mathrm{d}H - \frac{\tilde{H}}{2d\sqrt{d}} \frac{1}{M_{\mathrm{air}}} \frac{Z_{\mathrm{air}}}{Z} \mathrm{d}\bar{M} + \frac{\tilde{H}}{2d\sqrt{d}} \frac{\bar{M}}{M_{\mathrm{air}}^2} \frac{Z_{\mathrm{air}}}{Z} \mathrm{d}M_{\mathrm{air}} \\
& - \frac{\tilde{H}}{2d\sqrt{d}} \frac{\bar{M}}{M_{\mathrm{air}}} \frac{1}{Z} \mathrm{d}Z_{\mathrm{air}} + \left(\frac{\tilde{H}}{2d\sqrt{d}} \frac{\bar{M}}{M_{\mathrm{air}}} \frac{Z_{\mathrm{air}}}{Z^2} - \frac{H}{V^0 Z^2 \sqrt{d}} \right) \mathrm{d}Z
\end{aligned}$$

The factors preceding $\mathrm{d}H$, $\mathrm{d}\bar{M}$, $\mathrm{d}M_{\mathrm{air}}$, $\mathrm{d}Z_{\mathrm{air}}$ and $\mathrm{d}Z$ are the expressions for said sensitivity coefficients. M_{air} denotes the molar mass of air and Z_{air} its compressibility factor.

The uncertainty associated with the Wobbe index can now be calculated using the LPU from ISO/IEC Guide 98-3:2008 or ISO/IEC Guide 98-3/Supplement 2:2011 [6, 8] and the results from the first stage of the measurement model, providing values and standard uncertainties for H, $\bar{M}$ and Z as well the covariances between them.

9.3 Pairs of calorific values, molar masses and compressibility factors

9.3.1 In clause 8.4, a method was provided to obtain the covariance matrix associated with two compositions $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$, see equation (65). The method from clause 9.2 is extended to evaluate the covariance between pairs of calorific values, molar masses and compressibility factors, so that the covariances necessary when evaluating the uncertainty in the total energy as computed from equations (38) and (39).

9.3.2 Let

$$J_h = [h_1, \ldots, h_N] \tag{82}$$

and

$$J_M = [M_1, \ldots, M_N] \tag{83}$$

and

$$J_s = 2S\,[s_1, \ldots, s_N] \tag{84}$$

where

$$S = \sum_{i=1}^{N} x_i s_i$$

9.3.3 Consider two compositions $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ with covariance matrix $\boldsymbol{V}_{x_{12}}$, then the covariance matrix associated with the pair of calorific values $[H_1, H_2]^\top$, using the law of propagation of uncertainty, is given by [8]

$$\boldsymbol{V}_{\boldsymbol{H}_{12}} = J_{x,H}\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{H}}J_{x,H}^\top \tag{85}$$

where

$$J_{x,H} = \begin{bmatrix} J_h & \boldsymbol{0} & \boldsymbol{x}_1^\top \\ \boldsymbol{0} & J_h & \boldsymbol{x}_2^\top \end{bmatrix} \tag{86}$$

and

$$\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{H}} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \boldsymbol{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_H \end{bmatrix} \tag{87}$$

where $\boldsymbol{0}$ denotes an $N \times N$ matrix with zeros, $\boldsymbol{V}_{\boldsymbol{x}_1}$ the covariance matrix associated with $\boldsymbol{x}_1$, $\boldsymbol{V}_{\boldsymbol{x}_2}$ the covariance matrix associated with $\boldsymbol{x}_2$, $\boldsymbol{V}_{\boldsymbol{x}_{12}}$ the covariance matrix between $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ and $\boldsymbol{V}_{\boldsymbol{H}}$ the covariance matrix associated with the calorific values of the components $\boldsymbol{H}$.

9.3.4 For the molar mass, a similar set of equations can be developed. The covariance matrix associated with the pair of calorific values $[M_1, M_2]^\top$, using the law of propagation of uncertainty, is given by [8]

$$\boldsymbol{V}_{\boldsymbol{M}_{12}} = J_{x,M}\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{M}}J_{x,M}^\top \tag{88}$$

where

$$J_{x,M} = \begin{bmatrix} J_M & \boldsymbol{0} & \boldsymbol{x}_1^\top \\ \boldsymbol{0} & J_M & \boldsymbol{x}_2^\top \end{bmatrix} \tag{89}$$

and

$$\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{M}} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \boldsymbol{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_M \end{bmatrix} \tag{90}$$

where $\boldsymbol{V}_{\boldsymbol{M}}$ denotes the covariance matrix associated with the molar masses of the components $\boldsymbol{M}$.

9.3.5 For a pair of compressibility factor finally, the set of equations is as given below. The covariance matrix associated with a pair of compressibility factors $[Z_1, Z_2]^\top$ is given by

$$\boldsymbol{V}_{Z_{12}} = J_{x,s}\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{s}}J_{x,s}^\top \tag{91}$$

where

$$J_{x,s} = \begin{bmatrix} J_s & \boldsymbol{0} & \boldsymbol{x}_1^\top \\ \boldsymbol{0} & J_s & \boldsymbol{x}_2^\top \end{bmatrix} \tag{92}$$

and

$$\boldsymbol{V}_{\boldsymbol{x},\boldsymbol{s}} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \boldsymbol{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_s \end{bmatrix} \tag{93}$$

where $\boldsymbol{V}_{\boldsymbol{s}}$ denotes the covariance matrix associated with the molar masses of the components $\boldsymbol{s}$.

9.3.6 Considering that all other properties from ISO 6976 can be computed from H, M and Z, to compute correlation coefficients between any set of properties from this standard depending on H, M and Z, it is practical to calculate first the covariance matrix associated with the vector $\boldsymbol{\theta} = [H_1, H_2, M_1, M_2, Z_1, Z_2]^\top$. This covariance matrix is given by

$$\boldsymbol{V}_{\boldsymbol{\theta}} = J\boldsymbol{V}J^\top \tag{94}$$

where

$$J = \begin{bmatrix} J_H & \mathbf{0} & \boldsymbol{x}_1 & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & J_H & \boldsymbol{x}_2 & \mathbf{0} & \mathbf{0} \\ J_M & \mathbf{0} & \mathbf{0} & \boldsymbol{x}_1 & \mathbf{0} \\ \mathbf{0} & J_M & \mathbf{0} & \boldsymbol{x}_2 & \mathbf{0} \\ J_s & \mathbf{0} & \mathbf{0} & \mathbf{0} & \boldsymbol{x}_1 \\ \mathbf{0} & J_s & \mathbf{0} & \mathbf{0} & \boldsymbol{x}_2 \end{bmatrix} \tag{95}$$

and

$$\boldsymbol{V} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{V}_H & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \boldsymbol{V}_M & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \boldsymbol{V}_s \end{bmatrix} \tag{96}$$

9.3.7 For energy measurement on a volume basis, there are dependencies between Z and $\tilde{H}$, the calorific value a volume basis [4]

$$\tilde{H} = \frac{H}{ZV_0} \tag{97}$$

where $V_0 = RT/p$, where R denotes the ideal gas constant, T the temperature and p the pressure. Generally, V_0 is without uncertainty, as a reference temperature and pressure are used.

9.3.8 For the vector $[\tilde{H}, Z]^\top$, given the input vector $[H, Z]^\top$, the partial derivatives are given by

$$J = \begin{bmatrix} \frac{\tilde{H}}{H} & -\frac{\tilde{H}}{Z} \\ 0 & 1 \end{bmatrix} \tag{98}$$

9.3.9 Extending the calculation to two pairs of calorific values and compressibility factors can be done as follows. First, the covariance matrix associated with the vector $\boldsymbol{\theta} = [H_1, H_2, Z_1, Z_2]^\top$. This covariance matrix is given by

$$\boldsymbol{V}_{\boldsymbol{\theta}} = J\boldsymbol{V}J^\top \tag{99}$$

where

$$J = \begin{bmatrix} J_H & \mathbf{0} & \boldsymbol{x}_1 & \mathbf{0} \\ \mathbf{0} & J_H & \boldsymbol{x}_2 & \mathbf{0} \\ J_s & \mathbf{0} & \mathbf{0} & \boldsymbol{x}_1 \\ \mathbf{0} & J_s & \mathbf{0} & \boldsymbol{x}_2 \end{bmatrix} \tag{100}$$

and

$$\boldsymbol{V} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \mathbf{0} & \mathbf{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{V_H} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \boldsymbol{V_s} \end{bmatrix} \tag{101}$$

The covariance matrix associated with the vector $[\tilde{H}_1, \tilde{H}_2, Z_1, Z_2]^\top$ is then given by

$$\boldsymbol{V} = J \boldsymbol{V_\theta} J^\top \tag{102}$$

where

$$J_\theta = \begin{bmatrix} \frac{\tilde{H}_1}{H_1} & 0 & -\frac{\tilde{H}_1}{Z_1} & 0 \\ 0 & \frac{\tilde{H}_2}{H_2} & 0 & -\frac{\tilde{H}_2}{Z_2} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{103}$$

Instead of forming explicitly forming $\boldsymbol{V_\theta}$, the covariance matrix associated with the vector $[\tilde{H}_1, \tilde{H}_2, Z_1, Z_2]^\top$ can be calculated as

$$\boldsymbol{V} = J_\theta J \boldsymbol{V} J^\top J_\theta^\top \tag{104}$$

9.3.10 The calorific value on a mass basis is given by [4]

$$\bar{H} = \frac{H}{\bar{M}} \tag{105}$$

For energy measurement on a mass basis, the covariance matrix associated with a pair of calorific values $[\bar{H}_1, \bar{H}_2]^\top$ can be computed as follows. The covariance matrix associated with the vector $\boldsymbol{\theta} = [H_1, H_2, M_1, M_2]^\top$ is given by

$$\boldsymbol{V}_{\boldsymbol{\theta}_m} = J \boldsymbol{V} J^\top \tag{106}$$

where

$$J = \begin{bmatrix} J_H & \mathbf{0} & \boldsymbol{x}_1 & \mathbf{0} \\ \mathbf{0} & J_H & \boldsymbol{x}_2 & \mathbf{0} \\ J_M & \mathbf{0} & \mathbf{0} & \boldsymbol{x}_1 \\ \mathbf{0} & J_M & \mathbf{0} & \boldsymbol{x}_2 \end{bmatrix} \tag{107}$$

and

$$\boldsymbol{V} = \begin{bmatrix} \boldsymbol{V}_{x_1} & \boldsymbol{V}_{x_{12}} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{V}_{x_{12}} & \boldsymbol{V}_{x_2} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_{H} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{V}_{M} \end{bmatrix} \tag{108}$$

Then, the covariance matrix associated with $[\bar{H}_1, \bar{H}_2]^\top$ is given by

$$\boldsymbol{V}_{\bar{\boldsymbol{H}}} = J_{\theta_m} \boldsymbol{V}_{\boldsymbol{\theta}_m} J_{\theta_m}^\top \tag{109}$$

where

$$J_{\theta_m} = \begin{bmatrix} \frac{\bar{H}_1}{H_1} & 0 & -\frac{\bar{H}_1}{\bar{M}_1} & 0 \\ 0 & \frac{\bar{H}_2}{H_2} & 0 & -\frac{\bar{H}_2}{\bar{M}_2} \end{bmatrix} \tag{110}$$

10 Flow rate measurements

10.1 Volume flow

10.1.1 The volume flow rate is measured with a flow meter under field (metering) temperature and pressure conditions and should be converted to reference conditions before the energy can be calculated using equation (35). Following the methodology of OIML R140 [13], the volume flow rate at reference conditions when calculated from temperature, pressure and compressibility factor is

$$\dot{V}_0 = \frac{p T_0 Z_0}{p_0 T Z} \dot{V} \tag{111}$$

If the metering station is equipped with a densitometer, the volume flow rate at reference conditions is

$$\dot{V}_0 = \frac{\rho}{\rho_0} \dot{V} \tag{112}$$

where ρ denotes the density at field conditions and ρ_0 is the density at reference conditions calculated according to ISO 6976 [4].

10.1.2 The methods for evaluating the measurement uncertainty of temperature and pressure measurements are described in clauses 6 and 7, respectively. Similarly, the uncertainty in the compressibility factor can be estimated from the gas composition as described in clause 9. The focus in the following is therefore on the measurement of volume flow rate under field conditions.

10.1.3 The volume flow rate can be found by direct measurements with a dedicated volume flow meter or by indirect measurements with a mass flow rate meter or a differential pressure meter. If a mass flow meter is applied, the volume flow rate is calculated from the measured mass flow rate as

$$\dot{V} = \frac{\dot{m}}{\rho} \tag{113}$$

If a differential pressure flow meter (for example Venturi or Orifice), the volume flow rate is calculated from the measured differential pressure

$$\dot{V} = \frac{C}{\sqrt{1-\beta^4}} \varepsilon \frac{\pi}{4} d^2 \sqrt{\frac{2\Delta p}{\rho}} \tag{114}$$

where C denotes the discharge coefficient, β the ratio between the diameter of the throat (d) and the diameter of the pipe (D), ε is the expansibility factor and Δp is the differential pressure.

10.2 Mass flow

10.2.1 Mass flow rate is measured directly. typically using a Coriolis or thermal flow meter, or indirectly using a volume flow meter or differential pressure flow meter combined with gas density information. If the mass flow rate is determined using a volume flow meter, the mass flow rate is given by

$$\dot{m} = \rho \dot{V} \tag{115}$$

where ρ is the density at field conditions. If a differential pressure flow meter is used, the mass flow rate is calculated as

$$\dot{m} = \frac{C}{\sqrt{1-\beta^4}} \varepsilon \frac{\pi}{4} d^2 \sqrt{2\Delta p \rho} \tag{116}$$

The gas density can be found either by direct measured with a densitometer [50] or indirectly by application of equation of state calculations from the gas composition [4, 15, 27, 28]. The gas density at the same temperature and pressure conditions as the primary flow measurement shall be used to calculate the mass flow rate. Temperature and pressure measurements at field conditions are needed for the equation of state calculations of gas density, as well as for calculating the uncertainty of densitometer readings.

10.3 Uncertainty evaluation

10.3.1 The uncertainty evaluation presented in this subsection is valid for dedicated flow rate meters such as an ultrasonic flow meter or a turbine meter for volume flow or a Coriolis meter for mass flow.

10.3.2 The uncertainty model presented here is based on the model applied by the Norwegian Society for Oil and Gas Measurement [26] for flow meters with the flow rate under field conditions as the primary output. Typically, the flow meter will be flow calibrated at a calibration facility, followed by an adjustment of the meter to correct for systematic errors. The two main uncertainty contributors to the uncertainty of a flow calibrated meter are the calibration uncertainty and the field uncertainty as described by

$$u^2(Q) = u^2(Q_{\mathrm{cal}}) + u^2(Q_{\mathrm{field}}) \tag{117}$$

where $Q = \dot{m}$ for mass flow and $Q = \dot{V}$ for volume flow. If the flow meter is a dedicated volume flow meter, the flow quantity is volume flow rate at field (metering) conditions. If the flow meter is a dedicated mass flow meter, the flow quantity is mass flow rate.

10.3.3 The *calibration uncertainty* can be expressed as

$$u^2(Q_{\mathrm{cal}}) = u^2(Q_{\mathrm{cal,dev}}) + u^2(Q_{\mathrm{cal,ref}}) + u^2(Q_{\mathrm{cal,rep}}) \tag{118}$$

where

$u(Q_{\mathrm{cal,dev}})$ is the uncertainty of the correction factor estimate,

$u(Q_{\mathrm{cal,ref}})$ is the uncertainty of the reference measurement at the calibration facility, and

$u(Q_{\mathrm{cal,rep}})$ is the repeatability of the meter to be calibrated and the reference measurement.

10.3.4 The uncertainty of the correction factor estimate is calculated from the deviation of the actual flow rates measured by the flow meter and the reference meter at a series of actual flow rates. The uncertainty estimate will depend on the method that the correction is carried out, and will typically be lower for a linear interpolation correction between flow rates than a constant correction applied for all flow rates. The uncertainty of the reference measurement depends on the actual metering applied at the calibration facility. This is typically stated in the flow calibration certificate. The calibration repeatability is also found in the calibration certificate. This value covers both the repeatability of the flow meter and the repeatability of the reference meter. Typically, a linear interpolation between the repeatability at various flow rates is used.

10.3.5 The *field uncertainty* can be expressed as

$$u^2(Q_{\mathrm{field}}) = u^2(Q_{\mathrm{field,rep}}) + u^2(Q_{\mathrm{field,cond}}) + u^2(Q_{\mathrm{field,misc}}) \tag{119}$$

where

$u(Q_{\mathrm{field,rep}})$ is the repeatability of the flow meter at field conditions,

$u(Q_{\mathrm{field,cond}})$ is the uncertainty due to changes in conditions from calibration to field operation, and

$u(Q_{\mathrm{field,misc}})$ is additional uncertainties not eliminated by flow calibration.

10.3.6 The repeatability is typically found in the data sheet of the flow meter. The uncertainty due to changes in operating conditions depend on the actual installation and the functional operating principle of the flow meter. This include influencing factors such as dimensional changes in the meter body due to temperature and pressure changes, uncertainty due to calibration with other fluids than the true gas mixture, as well as changes in flow profile from calibration to field operation.

11 Temporal effects

11.1 Premable

11.1.1 Observations collected over time of the same quantity, e.g., the gas flow through a pipe, tend to be interrelated, the more so the smaller the time interval between observations. Often such a quantity is influenced by phenomena which themselves are a function of time.

EXAMPLE In gas grids, such phenomena can be, but are not limited to, the injection or withdrawal of gas, changes in process conditions (e.g., p, T) or blending with gases of other composition.

11.1.2 Time series models can be used to analyse series of observations made at equispaced epochs. An example of how such a model can be used is provided in ISO/IEC Guide 98-6:2021 [10, clause 11.7] for the temperature in a thermal bath.

11.1.3 Time series models should be applied to assess dependencies between the indications in a series of measurements. If such an analysis demonstrates that the indications are mutually independent, they can be modelled as such. In all other cases, a model should be chosen to describe the interrelationships between the indications.

11.1.4 A widely used class of time series models are the so-called auto-regressive moving average (ARMA) models. ARMA models express the value observed at a particular epoch as a linear combination of a finite number of past values (auto-regressive (AR) part) plus an error defined as a linear combination of measurement errors affecting the current observation and a finite number of previous observations (moving average (MA) part). ARMA models can be used to describe series of observations provided that the series and the fitted model satisfy the following two requirements.

1. The series of observations is stationary. In statistics, a (weakly) stationary time series is a finite variance process such that its mean value function is constant, and its auto-covariance function depends only on the distance between two data points, and not on the time at which the observations have been recorded.
2. The error terms of the fitted model behave like white noise with mean zero.

11.2 Checking the properties of the time series

11.2.1 Before performing any test or analysis to a series of data, it is good practice to plot the series to see the main features present in the data. This can be useful to, e.g., check if there are missing data or anomalous values in the time series.

11.2.2 The PDF of the measurement data can be compared to the resulting normal distribution fitted on the available data. This could be done visually or by computing the statistical distance, such as the Kullback-Leibler divergence or the Kolmogorov-Smirnov distance, between the two PDFs. A visual inspection of the sample PDF may be useful also to determine if multiple regimes have been recorded. This could be reflected in the sample PDF by, e.g., the presence of multiple peaks.

11.2.3 The Augmented Dickey Fuller (ADF) test is a statistical test commonly used to determine whether a time series is (weakly) stationary. The series is said to be stationary, if the null hypothesis can be discarded at the confidence level determined by a preset probability; in most applications, a 95 % confidence interval is considered. When performing the ADF test, it is possible to use a selection criteria such as Akaike's Information Criterion (AIC) or Bayesian Information Criterion (BIC) to select the number of lags to be included in the test. The default option in many publicly available data analysis libraries is AIC however, in applications where a small amount of data is available, it may be advisable to use BIC instead of AIC, since BIC takes the sample size into account.

11.2.4 The Shapiro test is a statistical test commonly used to determine whether the data are normally distributed. The data are said to be normally distributed if the null hypothesis cannot be discarded at the confidence level determined by a preset probabiity; in most applications, a 95 % confidence interval is considered.

11.3 Segmenting a series of observations

11.3.1 A requirement for the application of ARMA models is for the series of data to be statistically (weakly) stationary. If this is not the case, an option is to split the series at hand into shorter stationary sub-series. So-called change point methods can be used for this purpose [51]. These methods split the given series in sub-series according to detected changes in, e.g., the mean value or the empirical distribution. Therefore, depending on the selected criterion, different methods may detect different changing points.

11.3.2 Approximate methods, such as binary segmentation (BinSeg) [52], look at changes in the process's mean and are efficient methods to detect major changes in regime. If instead all regime changes are to be detected, exact methods such as Pruned Exact Linear Time (PELT) [53] should be employed.

11.3.3 Independently from the method used, it is good practice to check whether the resulting sub-series are stationary with normally distributed observations. If the newly defined sub-series satisfy the stationarity condition, an ARMA model can be fitted to describe the series.

11.3.4 Irrespective of the methods used to obtain the subseries, these subseries shall be long enough to fit a time series model.

11.4 Model selection

11.4.1 The order (i.e., the number of iterations to be included) of a pure MA process can be determined by checking the auto-correlation function (ACF), while the order of a pure AR model can be defined by analysing the partial auto-correlation function (PACF). In both cases, the number of lags with (partial) correlation value statistically different from zero should be included in the model.

11.4.2 In case of mixed models (i.e., models formed by a combination of MA and AR processes with order greater than 0), it is necessary to look both at the ACF and PACF. [54] provides some examples on how this can be done in practice. Commonly used model selection criteria such as corrected Akaike's Information Criterion (AICc) or BIC may be used to decide between mixed models of different orders. However, they should not be used to decide between, e.g., a mixed model and a purely MA (or AR) model. Such a decision should be made based on the physics being represented by the model, and the most sensible model from the point of view of the physics should be selected.

11.4.3 If multiple models are feasible from the point of view of the physics, instead of selecting a single model, they could be combined in some sort of averaging.

12 Combining time series analysis with uncertainty arising from measurement

12.0.1 In the metering of natural gas, biomethane, hydrogen and other energy gases, temporal effects as well as instrumental effects should be considered when calculating the total mass, volume or energy. The evaluation of temporal effects is described in clause 11 and provides insight as to whether the fluctuations in the quantities measured (e.g., temperature, pressure, volume, mass or calorific value) can be treated as independently distributed indications or that correlations need to be considered.

12.0.2 The correlations arising from instrumentation were described in clauses 6, 7, 8, 9 and 10. These correlations affect an entire time series and should be combined with those from time series analysis.

12.0.3 The equations for total volume (equation (35)), total mass (equation (32)) and total energy (equations (38) and (39)) contain only one quantity per epoch in the time series. To tie in the instrumental uncertainty in a time series analysis, the modelling framework of the GUM can be used, as laid down in ISO/IEC Guide 98-3 and ISO/IEC Guide 98-6 [6,10]. Introducing different quantities for the autocorrelation from time series analysis and for the effect of measurement instrumentation lets readily combine the corresponding uncertainty evaluations into the measurement model.

12.0.4 The introduction of different quantities for the uncertainty budget due to measurement instrumentation and the time series analysis can be performed in different ways. What is most practical depends on the shape of the measurement model describing the uncertainty budget of a single input quantity in the equation for the total volume, mass or energy. At this level, it is often evident how an input quantity for the indication of the instrument can be best integrated into the measurement model. Recalling, the indications, possibly corrected for, e.g., drift effects, are to be used in the time series analysis (see clause 11). From this analysis, estimates, standard uncertainties and correlation coefficients are obtained for these quantities.

12.0.5 Let us consider a simple additive measurement model

$$V_{\mathrm{tot}} = V_1 + V_2 \tag{120}$$

where V_{tot} denotes the total volume and V_1 and V_2 are the volumes passing a flow meter during subsequent time intervals Δt. The V_1 and V_2 are affected by uncertainty arising from the measuring instruments used [6,55]. In the absence of serial correlation between V_1 and V_2, the variance of V_{tot} is given by

$$u^2(V_{\mathrm{tot}}) = u^2(V_1) + u^2(V_2) + 2u(V_1, V_2) \tag{121}$$

where $u(V_1, V_2)$ denotes the covariance between V_1 and V_2.

12.0.6 If V_1 and V_2 are serially correlated, then this dependence should be taken into consideration. Let the revised measurement model take the form

$$V_{\mathrm{tot}} = V_1'\phi_1 + V_2'\phi_2 \tag{122}$$

where ϕ_1 and ϕ_2 are correction factors with mean 1 and standard uncertainty $u(V_1)/V_1$ and $u(V_2)/V_2$, respectively. The covariance $u(\phi_1, \phi_2) = u(V_1, V_2)/(V_1 V_2)$. The correction factors ϕ could be due to, e.g., the conversion of the volume measurement to normal conditions. The V_1' and V_2' are the recorded volumes as used in the time series analysis.

12.0.7 Using –again– the LPU, the variance of V_{tot} is given by

$$\begin{aligned} u^2(V_{\mathrm{tot}}) =& u^2(V_1') + u^2(V_2') + 2u(V_1', V_2') \\ &+ (V_1')^2 u^2(\phi_1) + (V_2')^2 u^2(\phi_2) + 2V_1'V_2' u(\phi_1, \phi_2) \end{aligned} \tag{123}$$

where $u(V_1', V_2')$ is the serial correlation determined using the methods presented in section 11, and thus a type A uncertainty; $u(\phi_1, \phi_2)$ is the correlation due to the instrumentation involved in determining the correction (e.g., flow meter, temperature and pressure sensors, gas chromatograph, equation of state) and thus a type B uncertainty. $u(\phi_1, \phi_2)$ could also include the uncertainty due to the time average approximation.

12.0.8 The covariance of a quantity that is the product of random variables (e.g., energy is the product between volume and calorific value) can be calculated using the formula by [56],

$$\begin{aligned}\mathrm{Cov}(XY, UV) = {} & \mathbb{E}[X]\mathbb{E}[U]\mathrm{Cov}(Y, V) + \mathbb{E}[X]\mathbb{E}[V]\mathrm{Cov}(Y, U) \\ & + \mathbb{E}[Y]\mathbb{E}[U]\mathrm{Cov}(X, V) + \mathbb{E}[Y]\mathbb{E}[V]\mathrm{Cov}(X, U) \\ & + \mathrm{Cov}(X, U)\mathrm{Cov}(Y, V) + \mathrm{Cov}(X, V)\mathrm{Cov}(Y, U)\,, \end{aligned} \tag{124}$$

where X, Y, U and V are random variables.

13 Uncertainty of totalized and average values

13.1 When accounting for quantity and energy in gas trading, it is necessary to determine their totalised or average values (see Sections 5.1 to 5.3). The calculation uncertainty component of these values depends both on the numerical procedure used to calculate them and on the nature of the observed quantities over time. In general, both deterministic and randomly varying quantities are present simultaneously, which poses additional challenges in estimating the calculation uncertainty.

13.2 Here, a method using separation of time variations of the observed quantity into the deterministic and random components using the time-domain filtering, followed by a separate analysis of calculation uncertainty for both components [57] is presented. This method enables the estimation of the calculation uncertainty over the entire accumulation time interval but also introduces certain effects of time-domain filtering on the correlation of the values in the random component. An outline of the proposed procedure for evaluating uncertainty associated with calculation of total/average from the time-sampled data is presented in Figure 1.

13.3 In the first step, time-domain signal processing is used to separate the deterministic and random components of the time-sampled input data, q_i, $i = 1 \ldots N$. Savitzky-Golay (S-G) filtering, a generalized moving average method based on least squares polynomial fitting across a moving window, is employed in this work. The setting parameters of the S-G filter are the order of the smoothing polynomial (set to 2 in this work) and the size of the smoothing window in terms of the number of samples N_{win} on either side of centre point (smoothing window contains $(2N_{\mathrm{win}} + 1)$ samples). The passed part of the signal is considered as the deterministic component, $q_{\mathrm{det},i}$, $i = 1 + N_{\mathrm{win}} \ldots\ N - N_{\mathrm{win}}$, and the removed part of the signal is considered as the random component $q_{\mathrm{ran},i} = q_i - q_{\mathrm{det},i}$, $i = 1 + N_{\mathrm{win}} \ldots\ N - N_{\mathrm{win}}$.

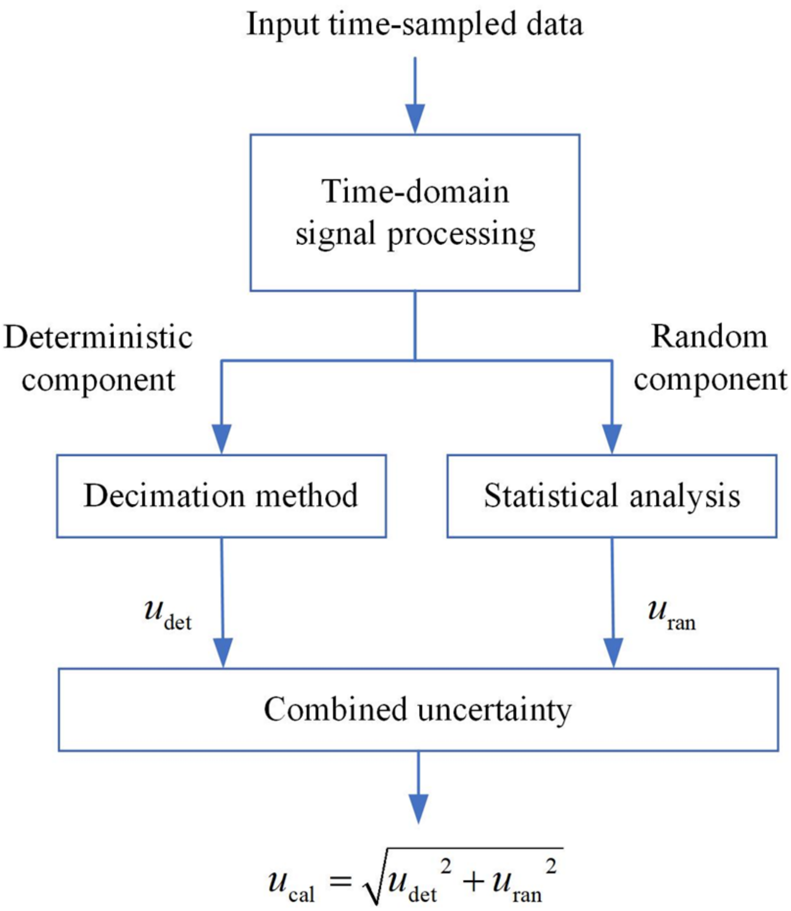

Figure 1: Schematic diagram of the procedure for evaluating the calculation uncertainty

13.4 The contribution to the totalization/averaging uncertainty, which is related to the numerical integration of the deterministic component $q_{\mathrm{det},i}$, is estimated using the decimation method. Decimation or downsampling with the decimation factor n_{dec} means that only every ${n_{\mathrm{dec}}}^{\mathrm{th}}$ sample is taken from the observed data $q_{\mathrm{det},i}$. The sought total/average Q is calculated for different decimation factors, $Q(n_{\mathrm{dec}})$, $n_{\mathrm{dec}} = 1 \ldots\ N_{\mathrm{dec}}$, and its dependence is least square approximated by the function $Q_{\mathrm{fit}}(n_{\mathrm{dec}}) = a\ n_{\mathrm{dec}} + b$. Here, the use of the linear function of n_{dec} is based on the assumption that the rectangle-rule numerical integration error is inversely proportional to the number of samples. The parameter $b = Q_{\mathrm{fit}}(0)$ is used as a prediction of the reference value for the case of infinite sample rate, and thus the numerical integration error is estimated as:

$$e_{\mathrm{det}} = Q(1) - Q_{fit}(0) \tag{125}$$

with the standard error associated with the estimate of the parameter b:

$$u\left(e_{\mathrm{det}}\right) = s\left(Q_{fit}(0)\right) \tag{126}$$

13.5 The standard uncertainty of calculation associated with the deterministic component is determined as:

$$u_{\mathrm{det}} = \sqrt{\left(\frac{e_{\mathrm{det}}}{\sqrt{3}}\right)^2 + u^2\left(e_{\mathrm{det}}\right)} \tag{127}$$

13.6 The contribution to the totalization/averaging uncertainty, which is related to the averaging of the random component, is estimated by statistical analysis. Without taking correlation effects into account, it is determined as:

$$u_{ran}^{(uncor)} = \frac{s\left(q_{ran,i}\right)}{\sqrt{N}} \tag{128}$$

and with consideration of correlation effects as:

$$u_{ran}^{(cor)} = \frac{s\left(q_{ran,i}\right)}{\sqrt{N}} \sqrt{1 + \frac{2\sum_{k=1}^{N_{cor}}\left(N_{ran} - k\right)\rho(k)}{N_{ran}}}, \tag{129}$$

where $\rho(k)$ is the k^{th} auto-correlation coefficient, N_{cor} is the number of considered auto-correlation coefficients and N_{win} is the number of samples of the separated random component. In this paper, N_{cor} is determined by identifying the smallest k for which $\rho(k) > 0$ and $\rho(k+1) < 0$.

13.7 Combined totalisation/averaging uncertainty, which considers the contributions related to deterministic and random components, is determined as:

$$u_{cal} = \sqrt{{u_{\mathrm{det}}}^2 + {u_{ran}}^2} \tag{130}$$

Annex A Conventions and notation

A.1 A generic quantity is denoted by an upper case letter and a measured value (estimate) by a lower case letter [7, Clause 4.8].

EXAMPLE 1 The measured value of the input quantity X_2 is denoted by x_2.

EXAMPLE 2 The measured value of the measurand Y is denoted by y.

A.2 A specific quantity is denoted by its agreed symbol. The measured value (estimate) is denoted by the same symbol adorned with a hat [7, Clause 4.8].

EXAMPLE 1 The thermodynamic temperature is denoted by T and a measured value of this temperature by $\widehat{T}$, for example $\widehat{T} = 295.4\,\mathrm{K}$.

EXAMPLE 2 The mass of a weight is denoted by m and the measured value by $\widehat{m}$.

A.3 The state of knowledge about a quantity is described by the probability density function (PDF) of a random variable denoted by the same symbol used for the quantity [7, Clause 4.1].

A.4 A PDF for more than one input quantity is often called joint even if all input quantities are mutually independent.

A.5 The PDF provided by the GUM uncertainty framework (GUF) is either a normal distribution with mean y and standard deviation $u(y)$ or a shifted and scaled Student t-distribution with mean y, scale $u(y)$ and effective degrees of freedom ν.

A.6 The law of propagation of uncertainty (LPU) applies to the use of a first-order Taylor series approximation to the model. The term is qualified accordingly when a higher-order approximation is used [7, Clause 4.9].

A.7 The notation $u(y)$ is to be read as the standard uncertainty associated with y. It represents the standard uncertainty about the true value of Y.

A.8 The terms “coverage interval” and “coverage probability” are used throughout this document. ISO/IEC Guide 98-3:2008 uses the term “level of confidence” as a synonym for coverage probability, drawing a distinction between “level of confidence” and “confidence level” [6, 6.2.2], because the latter has a specific definition in statistics. Since, in some languages, the translation from English of these two terms yields the same expression, the use of these terms is avoided here [7, Clause 4.11].

A.9 The subscript "c" [6, Clause 5.1.1] in $u_{\mathrm{c}}(y)$ for the combined standard uncertainty is deemed redundant and not used. Thus, the standard uncertainty associated with y is denoted generally as $u(y)$. Likewise, the qualifier "combined" is also regarded as superfluous [7, Clause 4.10].

A.10 Unless otherwise qualified, values are expressed in a manner that indicates the number of meaningful significant decimal digits [7, Clause 4.13].

A.11 Some symbols have more than one meaning in this document. See Annex B. The context clarifies the usage.

A.12 According to Resolution 10 of the 22nd CGPM (2003) "…the symbol for the decimal marker shall be either the point on the line or the comma on the line …". This document follows the convention of the Joint Committee for Guides in Metrology (JCGM) that has decided to adopt, in its documents in English, the point on the line as decimal marker [7, Clause 4.12].

Annex B List of symbols

d	relative density
$\boldsymbol{D}$	diagonal matrix
H	calorific value on a molar basis
$\bar{H}$	calorific value on a mass basis
$\tilde{H}$	calorific value on a volumetric basis
h	molar calorific value of a component
$\boldsymbol{I}$	identity matrix
M	molar mass of a component
$\bar{M}$	molar mass of a mixture
$\dot{m}$	mass flow rate
p	pressure
p_0	reference pressure
r	correlation coefficient
R	ideal gas constant
$\boldsymbol{R}$	correlation matrix
ρ	density
s	coefficient for calculating the compressibility factor according to ISO 6976
T	temperature
T_0	reference temperature
U	expanded uncertainty
u	standard uncertainty
$\dot{V}$	volume flow rate
$\boldsymbol{V}$	covariance matrix
x	amount fraction
$\tilde{x}$	non-normalised amount fraction
$\boldsymbol{x}$	composition (normalised)
Z	compressibility factor
Z_0	compressibility factor at reference conditions
$\mathbf{0}$	null matrix or vector
$\mathbf{1}$	vector containing ones

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Abbreviations

ACF auto-correlation function. 54

ADF Augmented Dickey Fuller. 53

AIC Akaike's Information Criterion. 53

AICc corrected Akaike's Information Criterion. 54

AR auto-regressive. 52, 54

ARMA auto-regressive moving average. 52–54

BIC Bayesian Information Criterion. 53, 54

BinSeg binary segmentation. 53

DSO distribution system operator. 6

EIV errors-in-variables regression. 32

GC gas chromatograph. 28, 29, 32

GUF GUM uncertainty framework. 59

GUM Guide to the expression of Uncertainty in Measurement. 3, 6, 7, 16, 26, 55

JCGM Joint Committee for Guides in Metrology. 60

LPU law of propagation of uncertainty. 6, 7, 12–14, 16, 19, 21–27, 32, 33, 35, 45, 55, 59

MA moving average. 52, 54

MCM Monte Carlo method. 6, 7, 12, 13, 19

MPE maximum permissible error. 12

OLS ordinary least-squares regression. 29, 32

PACF partial auto-correlation function. 54

PDF probability density function. 12, 13, 19, 53, 59

PELT Pruned Exact Linear Time. 53

TCD thermal conductivity detector. 28, 29

TSO transmission system operator. 6

WLS weighted least-squares regression. 29, 32

WTLS weighted total least-squares regression. 29, 32

Alphabetical index