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Posted Date: 7 November 2024

doi: 10.20944/preprints202411.0500.v1

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Credible Uncertainties for Natural Gas Properties Calculated from Normalised Natural Gas Composition Data

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Abstract: The evaluation of measurement uncertainty of natural gas properties calculated from composition data is an essential aspect of fiscal metering in the trade of natural gas. In particular in gas allocation, it is essential to have a reliable value for the uncertainty. This need is also reflected in the current edition of ISO 6976, the standard for computing natural gas properties, which follows much more closely the requirements of the "Guide to the expression of uncertainty in measurement". A critical aspect in the uncertainty evaluation of natural gas properties is the fact that the amount fractions of the components of natural gas are always correlated after normalisation. A novel algorithm is provided to recover these correlations from the normalised fractions and associated standard uncertainties. The standard uncertainties are reproduced within 2 %, which is acceptable for uncertainty calculations. The correlation coefficients obtained from the recovery algorithm agree with the ones obtained by normalisation. The algorithm requires only the data commonly stored by the natural gas industry as input and it enables providing values and credible associated uncertainties for natural gas properties calculated from composition.

Keywords: natural gas; ISO 6974; ISO 6976; calorific value; composition; correlation; measurement uncertainty; fiscal metering; custody transfer

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1. Introduction

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 [1–3]. The current edition of ISO 6976 [4], i.e., ISO 6976:2016, the documentary standard for calculating natural gas properties, takes on a more rigorous approach to the calculation of the measurement uncertainty of natural gas properties than its predecessor (ISO 6976:1995) [5]. ISO 6976:2016 takes the uncertainties associated with the pure substance enthalpies of combustion, the molar masses, and the compressibility factors of the components in natural gas at given reference pressure and temperature into account. Also, the propagation of the standard uncertainties and correlations of the natural gas are taken into account, as required by the Guide to the expression of Uncertainty in Measurement (GUM) [6,7].

Fundamental to these calculations is the availability of the natural gas composition. Both editions of ISO 6976 define the composition of natural gas as a series of (normalised) amount fractions of all components. Normalised amount fractions are always correlated [8,9], but the uncertainty structure can be different. For instance, the composition calculated from gravimetric gas mixture preparation, ISO 6142 [10,11] has a different uncertainty structure than the composition measured using gas chromatography in accordance with ISO 6974 [12,13] after normalisation.

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 [14]. Whereas it is recommended to provide measurement results with an uncertainty, and where relevant, also with covariances (or, equivalently, correlation coefficients) [6,15,16], 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 (see section 3).

doi:10.20944/preprints202411.0500.v1

In many uncertainty calculations in metrology, it is impossible to recover covariances without having a detailed insight in the underlying measurement models and uncertainty calculations. In the case of natural gas composition data, it is fortunate that there is an agreed method to normalise the data (described in ISO 6974 [12,13]). 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 2.

2. Normalisation of Composition

2.1. Normalised and Non-Normalised amount Fractions

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 [8]. This condition can be expressed as

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

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 [8].

A composition calculated from (gravimetric) gas mixture preparation [10,17] always meets the normalisation constraint (equation (1)), 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 must 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.

Ensuring that a composition expressed in amount fraction satisfies this condition can be achieved by using, e.g., the normalisation procedure from ISO 6974 [12,13], also known as *closure* of a composition [8]. The normalisation procedure is described in ISO 6974-1 [12] and the uncertainty calculation is given in ISO 6974-2 [13]. This procedure is the industry standard, but there are alternatives for carrying out a normalisation [18]. Considering that the set of amount fractions forming a composition can be expressed as a vector, a convenient way to express the associated uncertainty information is in the form of a covariance matrix [15].

The normalised amount fraction x_i is related to the raw amount fraction $\tilde{x}_i$ as follows [12,13]

$$x_i = \frac{\kappa \tilde{x}_i}{\sum_{j=1}^{n} \tilde{x}_j}. \tag{2}$$

The covariance matrix associated with the vector of the normalised amount fractions $\boldsymbol{x}$, $\boldsymbol{U_x}$, can be calculated from the covariance matrix $\boldsymbol{U_{\tilde{x}}}$ associated with the raw amount fractions as follows [15]

$$\boldsymbol{U_x} = \boldsymbol{C U_{\tilde{x}} C}^{\mathsf{T}}, \tag{3}$$

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

$$C_{ii} = \frac{\kappa}{\Xi} - \frac{\kappa \tilde{x}_i}{\Xi^2}, \tag{4}$$

$$C_{ij} = -\frac{\kappa \tilde{x}_i}{\Xi^2} \qquad (i \neq j), \tag{5}$$

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

The covariance matrix of a normalised composition has some special features. In each row (and column) the elements of $\boldsymbol{U_x}$ add to zero, which is a property of the uncertainty of a composition [8].

Equation (6) is a convenient way to verify whether the covariance matrix of a composition is valid for use in uncertainty calculations [8]. In matrix form, this check can be performed by verifying whether

$$\mathbf{1}^{\mathsf{T}}\boldsymbol{U}_x\mathbf{1} = 0, \tag{6}$$

where **1** denotes a column vector of length n, whose elements are all 1. Equation (6) is a direct consequence of the condition given in equation (1).

2.2. *Recovery Algorithm for the Covariances in a Normalised Composition*

The calculations in the previous section demonstrate that there are, at least *a priori*, cogent reasons for taking the correlations between the amount fractions in a normalised composition into account. Current industry practice is however that the normalised natural gas compositions are recorded and transmitted, and that the standard uncertainties associated with the fractions of the components are known from, e.g., validation of the analysis methods or the performance evaluation of the online natural gas analysers (see also ISO 10723 [14]). Usually, it is impossible to retrieve the full uncertainty structure of a set of variables from their values and standard uncertainties only.

In the case of a normalised composition however, it is possible to reconstruct the covariance matrix to a degree that it is suitable for the uncertainty calculations in ISO 6976 [4], provided that the normalisation was carried out as described in ISO 6974 [12,13]. In this work, this conventional normalisation [12, Definition 3.19] is chosen, as it is among the commonest methods applied in industry. The algorithm outlined shortly involves some matrix algebra, as a set of linear equations needs to be solved. As the emphasis of the modelling is on putting calculations into software systems, this is not considered a practical obstacle for its use.

The reconstruction of the covariance matrix is based on the considerations discussed in section 2. The expressions for the sensitivity coefficients (see equations (4) and (5)) 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 (8) and (9).

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 (3). For $u^2(x_k)$ this relationship reads as

$$u^2(x_k) = \sum_{j=1}^{n} C_{kj}^2 u^2(\tilde{x}_j), \quad k = 1, \dots, n. \tag{7}$$

The sensitivity coefficients can be approximated by

$$C'_{ii} \approx 1 - \frac{x_i}{\kappa}, \tag{8}$$

$$C'_{ij} \approx -\frac{x_i}{\kappa}, \qquad (i \neq j), \tag{9}$$

which follows from equations (4) and (5) by considering that $x_i \approx \tilde{x}_i$ for all i and $\Xi \approx \kappa$. Substituting equations (8) and (9) into the n equations (7) leads to a set of n linear equations where the $u^2(\tilde{x}_j)$ are the unknowns. This set can be represented as

$$\boldsymbol{A}\boldsymbol{v}_{\tilde{x}} = \boldsymbol{v}_x, \tag{10}$$

where $\boldsymbol{v}_x = \left(u^2(x_1), \dots u^2(x_n)\right)^{\mathsf{T}}$, and $\boldsymbol{v}_{\tilde{x}} = \left(u^2(\tilde{x}_1), \dots u^2(\tilde{x}_n)\right)^{\mathsf{T}}$. The elements of the matrix $\boldsymbol{A}$ are $A_{ij} = {C'_{ij}}^2$, where C' is given by equations (8) and (9).

The solution of equation (10) is given by $\boldsymbol{v}_{\tilde{x}} = \boldsymbol{A}^{-1}\boldsymbol{v}_x$, 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 [19]. Once the vector $\boldsymbol{v}_{\tilde{x}}$ is obtained, it can be converted to (an approximation of) the diagonal covariance matrix $\boldsymbol{U}_{\tilde{x}}$ and used in equation (3) to obtain the full covariance matrix $\boldsymbol{U}_x$.

3. Results

The recovery algorithm for the covariance matrix of the composition (see section 2.2) has been implemented in R [20]. The default solver for a set of linear equations is using the QR-factorisation. Consider the simple raw composition in Table 1. 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 1. Non-normalised composition of a natural gas containing 5 components, expressed in amount fractions (cmol mol^{-1})

Component	x cmol mol^{-1}	$u(x)$ 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 1 is used, i.e.,

$$\begin{aligned} \boldsymbol{x}^{\mathsf{T}} &= (3.280, 2.421, 84.335, 6.587, 3.378), \\ \boldsymbol{v}_x^{\mathsf{T}} &= (0.022^2, 0.019^2, 0.211^2, 0.044^2, 0.110^2). \end{aligned}$$

Solving the set of linear equations yields

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

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 1) is -0.97 %, which is acceptable for an uncertainty calculation. The covariance matrix $\boldsymbol{U}_x$ computed with the recovered values for the standard uncertainties differs negligibly from that computed directly from the data in Table 1. 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 2. 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 [16,21].

doi:10.20944/preprints202411.0500.v1

Table 2. Correlation matrices of the normalised composition (upper triangle) and from recovery (lower triangle)

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

In Table 3, a comparison is shown for selected natural properties calculated from ISO 6976, i.e., the molar calorific value, molar mass, the compressibility factors, and the calorific values on a mass and volume (real gas) basis for the three cases: (1) without covariances, (2) with the covariance matrix from normalisation according to ISO 6974 and (3) with the reconstituted covariance matrix. The metering and combustion temperatures are both 15 °C.

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

	With correlations		Recovery		Without correlations	
	x	$u(x)$	x	$u(x)$	x	$u(x)$
H	929.765	1.533	929.765	1.533	929.765	3.205
$\bar{M}$	18.984	0.030	18.984	0.030	18.984	0.062
Z	0.997 448	0.000 045	0.997 448	0.000 045	0.997 448	0.000 048
H_m	48.977	0.030	48.977	0.030	48.977	0.030
$\tilde{H}$	39.423	0.065	39.423	0.065	39.423	0.137

The calculated values are in all three scenarios identical. The calculated standard uncertainties with and without correlations are mostly vastly different. The only exception is the compressibility factor Z, for which the standard uncertainties in both scenarios are quite similar. Considering the correlations between the amount fractions leads generally to a $r$eduction of the standard uncertainty. The use of the recovered correlation matrix ("Recovery" in Table 3) provides identical values for the standard uncertainties for the statistically meaningful digits.

4. Conclusions

Using a normalised natural gas composition and a full covariance matrix are key to obtaining acceptable results with credible values for the uncertainties. While the assumption that the raw composition are mutually uncorrelated can be disputed, the approach for recovering the correlation matrix is a useful tool for processing measurement data in the natural gas industry, where often only the normalised composition of the metered natural gas is transmitted and the associated uncertainties of the amount fractions known, or approximately so.

The assumption that for measurement results from ISO 6974 the corresponding normalisation procedure had been used is reasonable. The sum of the raw amount fractions should lie between 98 cmol mol^{-1} and 102 cmol mol^{-1}, so that assuming that it does not deviate too much from 100 cmol mol^{-1} is fit for purpose for obtaining an acceptable approximation of the sensitivity matrix used in the recovery algorithm.

Finally, ISO 6976 should not entertain the idea of performing an uncertainty evaluation of natural gas properties while ignoring the correlations between the amount fractions of the natural gas composition. Not only is this idea contradicting the guidance in the GUM [6,15], it also leads for most parameters to a substantial overrating of the standard uncertainties.

Funding: This research was funded by the Ministry of Economic Affairs of The Netherlands. The APC was funded by MDPI.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declares no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

GUM	Guide to the expression of Uncertainty in Measurement
ISO	International Organisation for Standardisation
MDPI	Multidisciplinary Digital Publishing Institute

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