Differences in Uncertainty Calculation of Gas Parameters: Comparison of Different Standards and Analysis of the Effects of Normalisation and Covariance

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Content

Monte Carlo results using mean normalization of the gas composition vs. Standards

- *The two Monte Carlo approaches with mean normalization and run-by-run normalization give significantly different results. When run-by-run normalization is considered, covariance is applied, and the results are 2-3 times smaller than for the mean normalization approach.*
- *In most of the cases, the results obtained using the input uncertainties combined with CV_i as sensitivity coefficient, API 22.6 and ISO 6976:2016 combined with the unity matrix are comparable with the Monte Carlo method using the mean normalization approach.*

ISO 6976:2016 (Eq.1)

11.3.1 *"the correlation coefficients r(xi, xj) shall be taken as the elements of an identity matrix"*
Note: *"will usually **over-estimate the uncertainty** in each property"*

B.5 Molar-basis gross calorific value (eq. B.4)

$$u^2\left((Hc)_G\right) = \sum_{i=1}^{N}\sum_{j=1}^{N}\left[(Hc)_G^e\right]_i \cdot u(x_i)\cdot r(x_i,x_j)\cdot\left[(Hc)_G^e\right]_j \cdot u(x_j) + \sum_{i=1}^{N} x_i^2 \cdot u^2\left[\left((Hc)_G^e\right)_i\right]$$

11.4 Expanded Uncertainty (eq.26)

$$U(Y) = k \cdot u(Y)$$

"A coverage factor of k = 2 generally provides a level of confidence of approximately 95 %"

API MPM Ch 22.6:2015

GPA 2172:2009
10 Precision and Uncertainty
"The properties reported in this document […] are accurate to no better than 1 part in 1000."

AGA 8:2017
1.3.1 DETAIL Equation of State
"Region 1 in Table 1 shows […] the uncertainties in compressibility factors are less than 0.1 %"

8.3.6 Gross heating value uncertainty:

Let $z_i = y_i H_{v,i}$ $\quad H_v = \frac{\sum_i y_i H_{v,i}}{Z} = \frac{z_{sum}}{Z}$

$$U_{95}(z_i) = y_i H_{v,i}\sqrt{\frac{[U_{95}(y_i)]^2}{y_i^2} + \frac{[U_{95}(H_{v,i})]^2}{H_{v,i}^2}}$$

$$U_{95}(z_{sum}) = \sqrt{\sum [U_{95}(z_i)]^2}$$

$$U_{95}(H_v) = H_v\sqrt{\frac{[U_{95}(z_{sum})]^2}{z_{sum}^2} + \frac{[U_{95}(Z)]^2}{Z^2}}$$

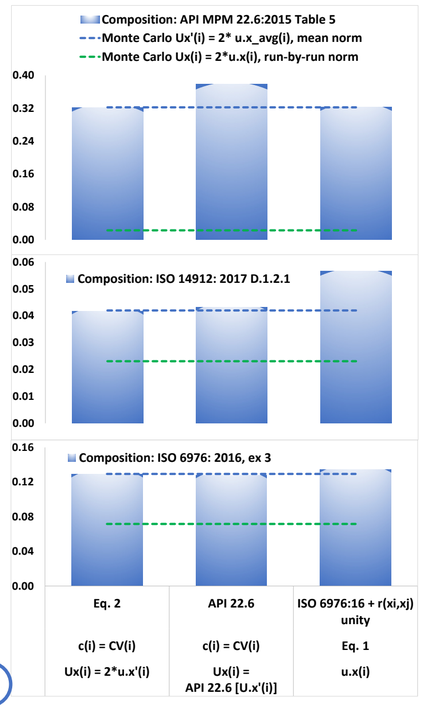
8.3.6 *"combined uncertainty of the measured, normalized mole fraction of component i, $U_{95}(y_{i,meas})$, […] Equation (12). Note that uncertainties in all unnormalized component concentrations ($x_{i,meas}$) are needed in order to calculate the uncertainty in a single normalized component concentration ($y_{i,meas}$)."*

$$U_{95}(y_{i,meas}) = y_{i,meas} * \sqrt{\frac{U_{95}^2(x_{i,meas})}{x_{i,meas}^2} + \frac{\sum_i U_{95}^2(x_{i,meas})}{\left(\sum_i x_{i,meas}\right)^2}}$$

Monte Carlo - mean normalization method [$u_{x_avg}(i)$]
- the randomized inputs generate unnormalized totals, that are **normalized after being averaged**
- the standard deviation per element is obtained from the input uncertainties
- covariance not considered

Sensitivity Coefficient: CV_i (Eq.2)

$$U_{CV} = \frac{2\cdot 100}{CVm}\sqrt{\sum_{i=1}^{n}\left[\left(\frac{x_i \cdot CV_i}{CVm}\cdot U_{x_i}\right)^2\right]}$$



Monte Carlo using run-by-run normalization of the gas composition vs. Standards

- *The method using sensitivity coefficient calculated as CV(i) – CVmix, is comparable with the Monte Carlo results obtained using run-by-run normalization data.*
- *The Norsok standard requires that the input uncertainties Of each component to be associated with normalized compositions. However, as seen in the bubble, if the input uncertainties are attributed to unnormalized composition, the uncertainty calculations show better agreement with Monte Carlo results, than using uncertainties recalculated for normalized compositions with ISO 6974-2:2001 or ISO 14912:2007.*
- *The difference between Monte Carlo with run-by-run normalization and the other calculation methods is < 0.01 %.*

Norsok I-106e1:2014

12.2.6.1 General
"All calculations are based on normalized values."

12.2.6.2.5 Gross Calorific Value
$U_{Hs} = [\Sigma(H_s - H_{si})^2 \times (U_{Xi}/100)^2]^{0.5}$
U_{Hs}- Uncertainty in gross calorific value per element, 95 %
H_S – Gross calorific value of mixture
H_{Si} – Gross calorific value per element

ISO 14912:2007

8.5.2.3 Normalization using a factor (eq. 67) $x_i = \frac{x_i'}{\sum_{k=1}^{N} x_k'}$

ISO 14912:2007
8.5.2.3 Normalization using a factor (eq. 68)

$$u^2(x_i) = \frac{(1-2x_i)u^2(x_i') + x_i^2\sum_{k=1}^{N} u^2(x_k')}{\left(\sum_{k=1}^{N} x_k'\right)^2}$$

ISO 6974-2:2001

5.6 Step 6: Calculation of normalized component mole fractions (eq 26) $x_i = \frac{x_i^*}{\sum_{w=1}^{q} x_w^*} \times (1 - x_{oc})$

5.7 Step 7: Calculation of normalized component standard deviations (eq 27)

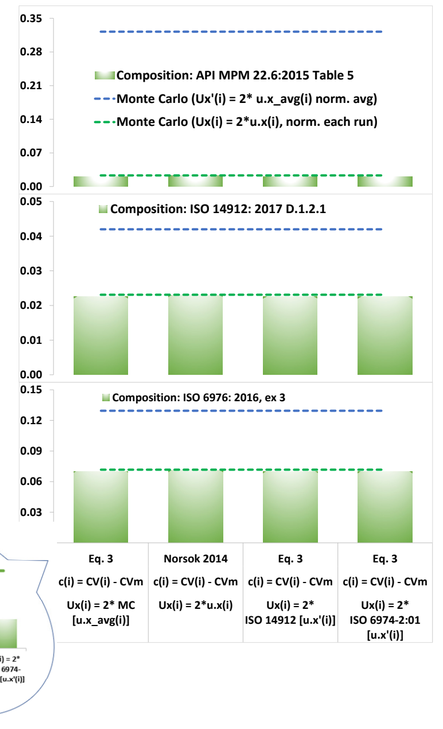
$$s(x_i) = x_i \times \sqrt{\frac{1-2x_i^*}{x_i^{*2}} \times s(x_i^*)^2 + \sum_{w=1}^{q} s(x_w^*)^2}$$

Monte Carlo – run-by-run norm method [u_x(i)]
- the randomized inputs generate unnormalized totals, that are normalized at **each run**, then the *standard deviation per element is recalculated*
- covariance considered

Sensitivity Coefficient: CV_i - CVm

$$U_{CV} = \frac{2\cdot 100}{CVm}\sqrt{\sum_{i=1}^{n}\left[(CV_i - CVm)\cdot u_{x_i}\right]^2}$$

Eq.3



Other uncertainty calculation methods that can't be correlated with the Monte Carlo results

*ISO:6976:1995 combined with the **repeatability** of each element, ISO 6976:2016 with correlation matrix, the relative method combined with ISO 6974-2:2001 or ISO 14912:2007 uncertainties for normalized composition give results that are most of the time between the two Monte Carlo calculation approaches.*

ISO 6976:2016 + ISO 14912:2007 (Eq.4)

ISO 6976:2016
11.3.1 Composition and compositional uncertainties
"b) mole fraction correlation coefficient (normalization) matrix"

ISO 14912:2007
8.5.2.3 Normalization using a factor (eq. 67) $x_i = \frac{x_i'}{\sum_{k=1}^{N} x_k'}$

ISO 14912:2007
8.5.2.3 Normalization using a factor (eq. 69)

$$u^2(x_i, x_j) = \frac{-x_i u^2(x_j) - x_j u^2(x_i) + x_i x_j \sum_{k=1}^{N} u^2(x_k)}{\left(\sum_{k=1}^{N} x_k'\right)^2}$$

ISO 14912:2007
8.5.2.3 Normalization using a factor (eq. 68)

$$u^2(x_i) = \frac{(1-2x_i)u^2(x_i') + x_i^2\sum_{k=1}^{N} u^2(x_k')}{\left(\sum_{k=1}^{N} x_k'\right)^2}$$

ISO 14912:2007
D.2.1.2 Establishing the initial molar composition and comp. uncertainty (eq. D.1) $r(x_i, x_k) = \frac{u(x_i, x_k)}{u(x_i)u(x_k)}$

ISO 6976:2016
B.5 Molar-basis gross calorific value (eq. B.4)

$$u^2\left((Hc)_G\right) = \sum_{i=1}^{N}\sum_{j=1}^{N}\left[(Hc)_G^e\right]_i \cdot u(x_i)\cdot r(x_i,x_j)\cdot\left[(Hc)_G^e\right]_j \cdot u(x_j) + \sum_{i=1}^{N} x_i^2 \cdot u^2\left[\left((Hc)_G^e\right)_i\right]$$

Monte Carlo [u_x(i)]
- the *standard deviation per element from the run-by-run normalization is recalculated* $s(x_i)$

Sensitivity Coefficient: CV_i

$$U_{CV} = \frac{2\cdot 100}{CVm}\sqrt{\sum_{i=1}^{n}\left[CV_i\left(u_{x_i}\right)\right]^2}$$

Eq.5

ISO 14912:2007
8.5.2.3 Normalization using a factor (eq. 68) $u^2(x_i) = \frac{(1-2x_i)u^2(x_i') + x_i^2\sum_{k=1}^{N} u^2(x_k')}{\left(\sum_{k=1}^{N} x_k'\right)^2}$
8.5.2.3 Normalization using a factor (eq. 67) $x_i = \frac{x_i'}{\sum_{k=1}^{N} x_k'}$

ISO 6974-2:2001
5.7 Step 7: Calculation of normalized component standard deviations (eq 27) $s(x_i) = x_i \times \sqrt{\frac{1-2x_i^*}{x_i^{*2}} \times s(x_i^*)^2 + \sum_{w=1}^{q} s(x_w^*)^2}$
5.6 Step 6: Calculation of normalized component mole fractions (eq 26) $x_i = \frac{x_i^*}{\sum_{w=1}^{q} x_w^*} \times (1 - x_{oc})$

ISO 6976:1995

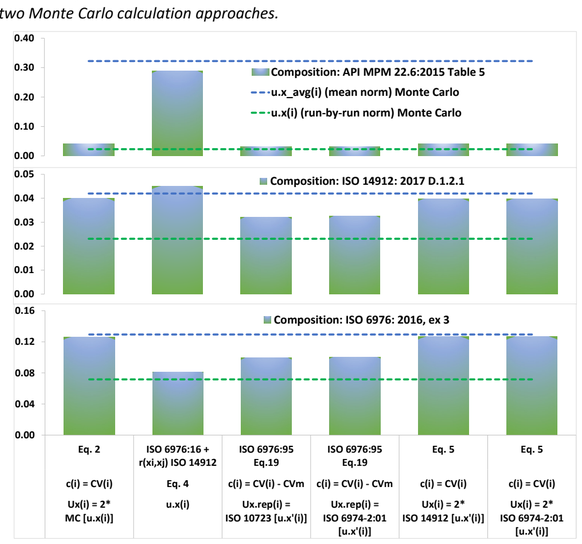
ISO 6974-2:2001
5.9 Relationship between ISO 6974-2 and ISO 6976 / 5.9.2 Non-normalized mole fraction (x_i^*)
"Repeatability of the standard deviations": $r_i^* = 2\sqrt{2} \times s(x_i^*)$ where $\Delta x_i^* = r_i^*$

ISO 10723:2002
6.2.2 Procedure: $r(x_i) = 2{,}8 s(x_i)$
Repeatability (absolute) for not-normalized compositions
- *"expected to agree on 95 % of occasions" -A.6.1*

ISO 6976-1995
9.1.2 (+ Annex H) Repeatability and Reproducibility
"b) When all components including methane are analysed, then

$$\Delta H_{mix}^* = \left\{\sum_{j=1}^{N}\left[\Delta x_j^* \cdot (H_j^* - H_{mix}^*)\right]^2\right\}^{1/2} \quad \ldots(19)$$

H_{mix}^* is calculated using the normalized mole fractions x_j. Δx_j^* is the repeatability of the mole fraction of component j in the mixture of N components before normalization is carried out."



ISO 6974:2:2012: Uncertainty of normalized composition & normalization methods

- *The results obtained by using the uncertainty of the normalized composition calculated with ISO 6974-2:2012 are considerably higher than any other results.*
- *The standard proposes **two normalization methods**: mean normalization and run-by-run normalization, similar to the two Monte Carlo approaches.*

Monte Carlo - mean normalization method [$u_{x_avg}(i)$] covariance not considered

Monte Carlo – run-by-run normalization method [u_x(i)] - covariance considered

ISO 6974-1&2:2012

ISO 6974-1
6.9 Step 8: Type of Normalization
Mean / Run-by-run

ISO 6974-1
6.9.1 - 6.9.2 *"a) **Mean normalization**: The repeat analyses for each component are averaged to form a series mean and then normalized."*

ISO 6974-2
5.3 Step 9 – Calculation of uncertainty of mole fractions (a)
"1) mean peak analyser response from all runs;
2) raw mole fraction;
3) normalized mole fraction."

ISO 6974-2
5.3.2.3 Uncertainty of normalized mole fractions (eq 5, 10, 11)

$$u^2(x_i) = \sum_{s=1}^{xsmp}\left[\left[C_j(x_i, x_s^*)\right]^2 u^2\left(x_s^*\right)\right] + \left[C_j(x_i, x_{oc})\right]^2 u^2(x_{oc})$$

$$C_j(x_i, x_s^*) = \frac{\partial x_i}{\partial x_s^*} = \frac{T - x_i^*}{T^2}(1 - x_{oc})$$

$$C_j(x_i, x_{oc}) = \frac{\partial x_i}{\partial x_{oc}} = -\frac{x_i^*}{T}$$

x – normalised mole fraction, ***x**** - raw mole fraction, ***T*** – unnormalized total

ISO 6974-2
5.4 Step 10 – Calculation of the expanded uncertainty of mole fractions (eq 22)

$$U(x_i) = k \times u(x_i)$$

"A coverage factor of k = 2, providing a level of confidence of approximately 95 %, is usually used."

ISO 6974-1
6.9.1 - 6.9.3 *"b) **Run-by-run normalization**: Each repeat analysis is normalized independently; the average of these normalized values is then calculated."*

ISO 6974-2
5.3 Step 9 – Calculation of uncertainty of mole fractions (b)
"1) raw mole fraction for each run;
2) normalized mole fraction for each run;
3) mean normalized mole fraction."

ISO 6974-2
5.3.3.3 Uncertainty of normalized mole fractions (eq 16, 20, 21)

$$u^2(\bar{x}_i) = \frac{\sum_{r=1}^{runs}\left[\sum_{s=1}^{xsmp}\left[\left[C_i(x_{ij}, x_{sj}^*)\right]^2 u^2(x_{sj}^*)\right] + \left[C_i(x_{ij}, x_{oc})\right]^2 u^2(x_{oc})\right]}{n_j^2}$$

$$C_i(x_{ij}, x_{sj}^*) = \frac{\partial x_{ij}}{\partial x_{sj}^*} = \frac{T_j - x_{ij}^*}{T_j^2}(1 - x_{oc})$$

$$C_j(x_{ij}, x_{oc}) = \frac{\partial x_{ij}}{\partial x_{oc}} = -\frac{x_{ij}^*}{T_j}$$

x – normalised mole fraction, ***x**** - raw mole fraction, ***T*** – unnormalized total, n_j – total number of injections

Sensitivity Coefficient: CV_i

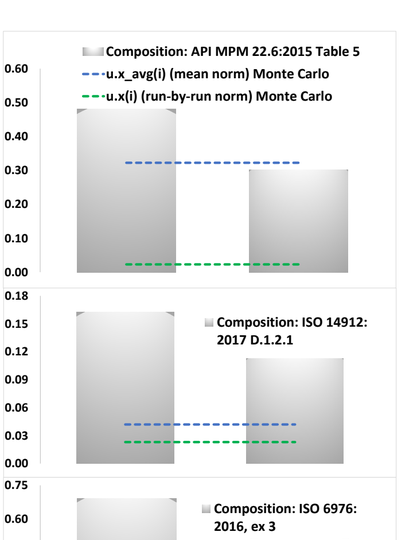
$$U_{CV} = \frac{2\cdot 100}{CVm}\sqrt{\sum_{i=1}^{n}\left[CV_i\left(u_{x_i}\right)\right]^2}$$

Eq.5

Sensitivity Coefficient: CV_i - CVm

$$U_{CV} = \frac{2\cdot 100}{CVm}\sqrt{\sum_{i=1}^{n}\left[(CV_i - CVm)\cdot u_{x_i}\right]^2}$$

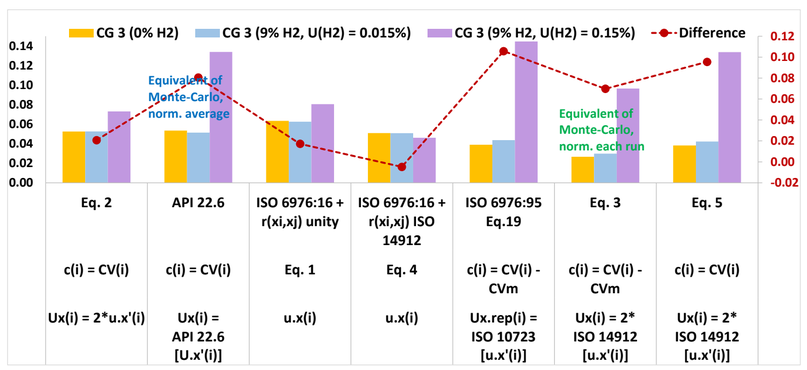
Eq.3

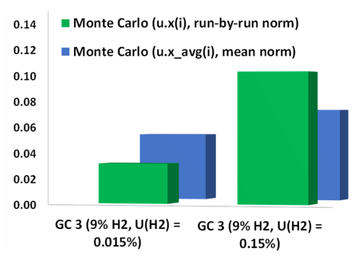


Gas compositions with Hydrogen. What do standards say?

- *When compared to the uncertainty of a gas composition without H_2, the uncertainty of the calorific value of the mix with 10 – 20 mol % H_2 will be:*
  - *slightly higher, if the $U(H_2)$ < uncertainty of the other dominant elements*
  - ***considerably higher**, if the $U(H_2)$ >> uncertainty of the other dominant elements.*

Standard	Hydrogen Content
ISO 6975:1997	Section 1: **0,001 % to 0,5 %**
ISO 6974-1:2012	Annex A Table A.1: **0,01 to 0,5 mol %**
ASTM D-1945	Appendix X1.1: **0.01 to 10 mol %**
Norsok I-106	H2 is not mentioned in section 12.1 where the applicable components ranges are provided
ISO 10723:2002	H2 is not mentioned in Annex A.1 where the applicable components ranges are provided
API MPM Ch. 22.6:2015	Composition requirements not mentioned
ISO 6976_1995	Section 1 Scope: *except for C1, C2, CO2 and N2* "***no other component should exceed 0.05 mole fraction***" *"Given these limits, the expected trueness of the calculation is within 0.1 %."*
ISO 6976_2016	Section 1 Scope: *"Note 2: There are **no explicit limits of composition** […]. However, the restriction of volume-basis calculations to mixtures with a compression factor greater than 0.9 at reference conditions sets implicit limits on composition."*
AGA 8-Part 1:2017 (DETAIL and GROSS)	Section 1.3.1, Table 1 - Detail Eq. of State: **Range A: < 5%; Range B: < 100 %; Range C: < 1 %** Section 1.3.2, Table 2 - Gross Eq. of State: **Range 1: < 0.2%; Range 2: < 2 %**
AGA 8-Part 2: 2017 (GERG)	Section 5, Table 5: **Pipeline quality range: < 10 %; Intermediate quality range: < 40 %**



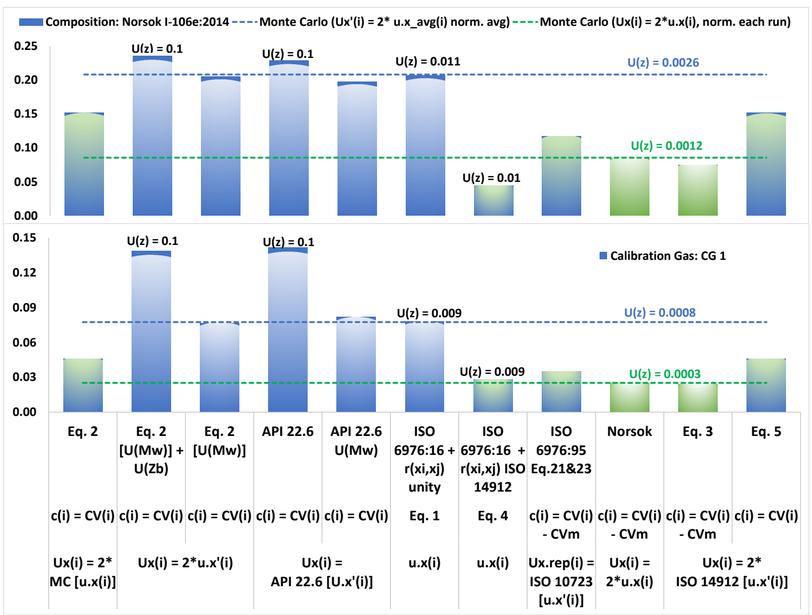


If $U(H_2)$ > U(C1) when the concentration of C1 < H_2 < C2 < C3 < … mol %, the *Monte Carlo uncertainty with run-by-run normalization* will be higher than the *Monte Carlo uncertainty with mean normalization* (opposite effect).

Compressibility effect on the uNcertainty of real gas properties

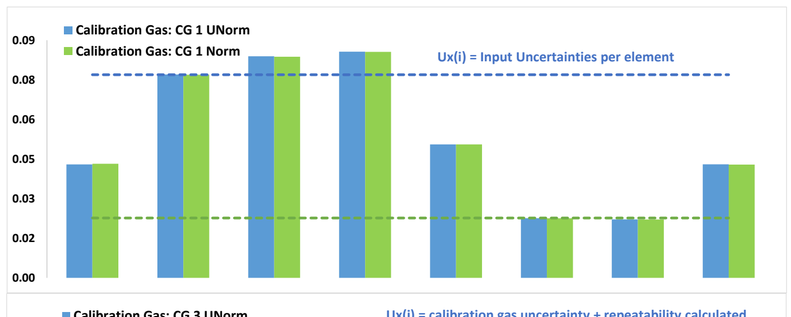
- *The standard deviation of the compressibility uncertainty calculated with both Monte Carlo approaches is very small and considerably different from the values provided for different regions in AGA 8 or calculated with ISO 6976:2016 equation.*
- *The AGA 8 suggested values for the compressibility uncertainties can have either a significant or a minor impact on the real gas calculations, depending on the magnitude of the uncertainty for ideal gas.*

Standard	Compressibility Uncertainty
API MPM Ch. 22.6:2015	8.3.7 *"The compressibility factor Z is to be computed using the AGA-8 equation of state. For most gas streams of interest, the value of Z computed by AGA-8 carries a relative uncertainty of **0.1 % of value**."*
ISO 6976_1995	9.1.2 *"NOTE 19 The contribution of the repeatability ΔZ of the calculated compression factor z to the overall repeatability ΔH of the calorific value on a volumetric basis is small, and is therefore ignored in the above formulation; likewise, the contribution of ΔZ to the overall repeatability Δp of the real gas density […] **is also ignored**."*
ISO 6976_2016	B.4 Compression Factor $u^2(Z) = 4 \cdot s^2 \times \left(\left[\sum_{i=1}^{N}\sum_{j=1}^{N} s_i \cdot u(x_i)\cdot r(x_i,x_j)\cdot s_j \cdot u(x_j)\right] + \sum_{i=1}^{N} x_i^2 \cdot u^2(s_i)\right)$
Norsok I-106	12.2.6.2.6 Density/molecular mass: *"When the composition is used for density calculation, the resulting uncertainty in molar mass, UM, shall be less than 0,20 %"*
AGA 8-Part 1:2017	Figure 1: Range 1 = 0.1%; Range 2 = 0.3 %; Range 3 = 0.5 %; Region 4 = 1 %
Monte-Carlo	Calculated as standard deviation, U(z) << 0.01 % (k = 2)



Input composition normalized vs. unnormalized – does it make a difference in the calorific value uncertainty?

- *When calculating the uncertainties, attention should be paid to the **input uncertainties**, if they are expressed for normalized or unnormalized compositions and the confidence level.*
- *As for the composition itself, the difference between the uncertainty results is **insignificant** if it was calculated with normalized or unnormalized composition.*
- *All calculation results are dependent on composition and component uncertainties. If one of the components with higher concentrations has also a higher uncertainty associated, exceptions can be observed when comparing different approaches.*
- *Based on all the different results, it's important to know the specifics of the standards in use and based on the normalization method used, to apply standard accordingly.*



U(unorm) - U(norm)							
CG 1	-0.0001	0.0001	0.0002	0.0001	0.00002	0.00002	0.00005	0.0001
CG 3	-0.006	-0.003	-0.008	-0.003	-0.003	-0.005	-0.009	-0.007

Looking for an answer to the following questions:
- ✓ Which of the two Monte Carlo approaches should be used and when?
- ✓ How to choose the right uncertainty calculation method?
- ✓ Should the correlation matrix provided in ISO 14912 be reviewed?
- ✓ Why are the uncertainty results obtained with ISO 6974-2:2012 so different from all other standards used?
- ✓ Is uncertainty of the compressibility important to be considered in calculations?