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Gas mixtures — Gravimetric preparation — Mastering correlations in composition

Mélanges de gaz — Préparation gravimétrique — Maîtrise des corrélations en composition

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Foreword

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ISO/TS 29041 was prepared by Technical Committee ISO/TC 158, *Analysis of gases*.

This document is not to be regarded as an “International Standard”. It is proposed for provisional application so that information and experience of its use in practice may be gathered. Comments on the content of this document should be sent to the ISO Central Secretariat.

Introduction

ISO/TC 158 decided at its meeting in Prague (October 2002) to investigate the influence of possible correlations (both extrinsic and intrinsic) on the uncertainty calculation(s) for mixture composition and gas mixture property data. Methods should be developed for taking all existing correlations into account, and exemplified appropriately.

This Technical Specification describes the tools needed for full accounting of correlations, and exemplifies how these tools should be applied to practical examples. Some recommendations are given which are intended to provide support to the decision on whether or not, and in which situations, the full calculatory scheme as described herein should be applied in practice, and in which situations simplified approaches as given in ISO 6142 are considered sufficient for the intended purpose.

Gas mixtures — Gravimetric preparation — Mastering correlations in composition

1 Scope

In this Technical Specification, the gravimetric mixture preparation as given in ISO 6142 is investigated for influences of *a priori* existing, as well as correlations introduced by data processing.

All calculations refer to an example which consists in the preparation of a synthetic natural gas of a target composition as follows: 1,4 mol % N_2, 1,8 mol % CO_2, 9,4 mol % ethane, 3,4 mol % propane, 1 mol % *n*-butane, and 83 mol % methane.

All considerations given for this example concerning mixture feasibility, choice of preparation procedure, and weighing steps and sequences are the same as given in ISO 6142. This also applies to all estimates for basic uncertainty sources and the purity tables of the gases used for preparation.

All calculations follow the principles, and use the tools and algorithms laid down in Annex A. For the sake of simplicity, procedural steps such as matrix transformation, inversion or matrix calculus are not detailed each time they are used in the calculations.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

3 Symbols and abbreviated terms

CV_i	calorific value of gas component i, $i = 1, \ldots, n$
CV	calorific value of the gas mixture
$\boldsymbol{G}$	system of model equations describing the measurand
$\boldsymbol{J}$	Jacobian
m	mass
m_g	mass of the gas component in the mixture cylinder, as determined by gravimetry
m_m	mass difference, as determined, between mixture and reference cylinder after the corresponding filling step
m_x	mass difference corrected between mixture and reference cylinder after the corresponding filling step

M_i	molar mass of gas component i, $i = 1, \ldots, n$
M	molar mass of the gas mixture
$\boldsymbol{Q}$	transfer matrix
$U(x)$	expanded uncertainty of a value x
$u(x)$	standard uncertainty of a value x
$u^2(p_i, p_j)$	variance (for $i = j$) of a value p_i, or covariance (for $i \neq j$) of two values p_i and p_j
u_B	buoyancy correction (see Note)
u_exp	correction accounting for cylinder expansion
u_m	uncertainty of balance indication (cumulated estimate)
u_R	correction for residual gas in the cylinder after evacuation
$\boldsymbol{V}$	variance/covariance matrix for a set of results or parameters
w_g	mass fraction of a component as determined by gravimetry
x_i	mole fraction of gas component i in the final mixture, $i = 1, \ldots, n$
$x_{i,k}^\mathrm{pur}$	mole fraction of gas component k in pure gas i used for gravimetric preparation

NOTE ISO 6142 uses symbols with lower-case letter "u" (e.g. u_B) for variables other than uncertainties, namely for corrections made for influential factors in the gravimetric mixture production process, e.g. buoyancy. This symbol assignment to variables is also retained for the purposes of this document. The reader should be careful not to confound values and value uncertainties. The uncertainty of, say, u_B is $u(u_\mathrm{B})$.

4 Mixture preparation by gravimetry

For the weighing steps and sequence as described in the example, the values for the m_x and their corresponding uncertainties (as given in Table 1) can be obtained from the raw data and uncertainty source estimates.

Estimates for the corrections and their uncertainties are the same as in the CO in N_2 example in ISO 6142.

Table 1 — Component weighing data and their uncertainties for the gas mixture

Masses and their uncertainties	Component						
	Vacuum	***n*-Butane**	**Propane**	**Ethane**	CO_2	N_2	**Methane**
m_{m} [g]	50,000 21	37,999 302	7,999 707	50,000 21	65,999 937	73,999 78	345,998 422
u_{m} [g]	−0,011	0,157	−0,731	−0,299	0,052	0,065	0,13
u_{B} [g]	0,007 45	0,005 66	0,001 19	0,007 45	0,009 84	0,001 1	0,051 58
u_{exp} [g]					0,001 49		0,015 9
u_{R} [g]							0,003 3
$u(m_{\mathrm{m}})$ [mg]	0,015	0,019 3	0,010 8	0,015	0,020 2	0,015 1	0,06
$u(u_{\mathrm{m}})$ [mg]	2,3	2,3	2,3	2,3	2,3	2,3	2,3
$u(u_{\mathrm{B}})$ [mg]	0,019	0,014	0,003	0,019	0,025	0,028	0,13
$u(u_{\mathrm{exp}})$ [mg]					0,86		9,16
$u(u_{\mathrm{R}})$ [mg]							1,9
m_x [g]	49,996 660	38,161 962	7,269 897	49,708 660	66,063 267	74,065 880	346,199 202
$u(m_x)$ [mg]	2,300 128	2,300 124	2,300 027	2,300 127	2,455 735	2,300 220	9,634 630

The following reasoning applies to possible correlations: it is assumed that u_{m} is a random variable governed by a common distribution, and each realisation is a drawing from the distribution. Under this assumption, there is no reason for making allowances for correlation(s) since the realisations are independent. The uncertainty sources for the u_{B} estimates are the same, namely pressure, temperature, and humidity. This causes correlation, but the common sources are not quantified in ISO 6142. There is no reason for assuming correlations for the u_{exp} estimate, and u_{R} occurs only once for methane. For m_{m}, a clear correlation exists since the same mass pieces are used, but their combinations are unknown (except for some cases). Usually, these correlations are small and may be neglected in practice. Here, for demonstrating the principle of the method they are included where obvious. The corresponding variance-covariance matrix for the data table is given in Table 2.

Table 2 — Variance-covariance matrix for the weighing data in Table 1

$V(m_x)$	**Vacuum**	***n*-Butane**	**Propane**	**Ethane**	CO_2	N_2	**Methane**
Vacuum	5,290 586	0	0	0,000 225	0,000 225	0,000 225	0
n-Butane	0	5,290 568 49	0	0	0	0	0
Propane	0	0	5,290 125 64	0	0	0	0
Ethane	0,000 225	0	0	5,290 586	0,000 225	0,000 225	0
CO_2	0,000 225	0	0	0,000 225	6,030 633 04	0,000 225	0
N_2	0,000 225	0	0	0,000 225	0,000 225	5,291 012 01	0
Methane	0	0	0	0	0	0	92,826 1

Values in Table 1 are exemplified for the N_2 column: The uncertainty of the m_x value for N_2 is combined from the contributing sources of uncertainty according to the usual uncertainty propagation rule. It holds

$$u^2(m_x) = u^2(m_\mathrm{m}) + u^2(u_\mathrm{m}) + u^2(u_\mathrm{B}) \tag{1}$$

delivering a value of 2,300 3 mg. The corresponding variance is 5,291 012 01 mg^2 and contained in the sixth row of the N_2 column. The m_m values for the N_2 and the methane filling step are quite different, it was assumed that different mass pieces were used. Other common sources of uncertainty are the corrections u_m and u_B for which either an absence of correlation is assumed, or the correlations are negligible or unknown. Thus, the covariance term is set to zero (seventh row of the N_2 column). The same reasoning holds for the *n*-butane/N_2 and the propane/N_2 pairs (second and third row of the N_2 column).

The m_m values for the initial weighing (vacuum) and the ethane and CO_2 filling step are quite similar or at least in the region of 50 g, so it can be assumed that the same mass pieces were used. For simplicity, the covariance arising from this instance was estimated as the variance $u^2(m_\mathrm{m})$ of the initial weighing of the mixture cylinder containing only vacuum [$u(m_\mathrm{m}) = 0{,}015$ mg, $u^2(m_\mathrm{m}) = 0{,}000\,225\ \mathrm{mg}^2$]. It is the same for all three pairs (first, fourth and fifth row of the N_2 column). Note that the values which appear in rows 1 to 7 in the N_2 column are repeated in columns 1 to 7 of the N_2 row since variance-covariance matrices are symmetric.

From the set of equations:

$$m_\mathrm{g}(\mathrm{butane}) - m_\mathrm{vac} + m_\mathrm{butane} = 0$$

$$m_\mathrm{g}(\mathrm{propane}) - m_\mathrm{butane} + m_\mathrm{propane} = 0$$

$$m_\mathrm{g}(\mathrm{ethane}) - m_\mathrm{propane} - m_\mathrm{ethane} = 0$$

$$m_\mathrm{g}(\mathrm{CO_2}) - m_\mathrm{CO2} + m_\mathrm{ethane} = 0$$

$$m_\mathrm{g}(\mathrm{N_2}) - m_\mathrm{N2} + m_\mathrm{CO2} = 0$$

$$m_\mathrm{g}(\mathrm{methane}) - m_\mathrm{methane} + m_\mathrm{N2} = 0$$

the transfer matrix $\boldsymbol{Q}$ is formed according to the recipes given in Annex A, and the gas masses and the variance-covariance matrix of the mixture composition are calculated from the m_x data of Table 1 and the variance-covariance matrix in Table 2. This yields the values given in Table 3.

Table 3 — Gas masses in the mixture, their uncertainties and the variance-covariance matrix

	n-**Butane**	**Propane**	**Ethane**	CO_2	N_2	**Methane**
m_g [g]	11,834 698	30,892 065	56,978 557	16,354 607	8,002 613	272,133 322
$u(m_\mathrm{g})$ [mg]	3,252 869	3,252 798	3,252 801	3,364 635	3,364 698	9,905 408
V	*n*-**Butane**	**Propane**	**Ethane**	CO_2	N_2	**Methane**
n-Butane	10,581 154	−5,290 568 5	0,000 225	0	0	−0,000 225
Propane	−5,290 568 5	10,580 694	−5,290 125 6	0	0	0
Ethane	0,000 225	−5,290 125 6	10,580 712	−5,290 361	0	−0,000 225
CO_2	0	0	−5,290 361	11,320 769	−6,030 408	0
N_2	0	0	0	−6,030 408	11,321 195	−5,290 787 01
Methane	−0,000 225	0	−0,000 225	0	−5,290 787	98,117 112

5 Unit conversion

The above composition is given as gas masses in grams (uncertainties in milligrams) and should now be converted to mol/mol. This will also enable the inclusion of purity data which are given in the tables in mol/mol. Calculations are carried out using CONVERT [1] and yield the mole fractions and variance-covariance matrix shown in Table 4. See also ISO 14912 [2] for more details on the mathematical and computational background.

Table 4 — Component mass fractions in the mixture, their uncertainties and the variance-covariance matrix

	n-Butane	Propane	Ethane	CO_2	N_2	Methane
w_g	0,009 971 64	0,034 308 29	0,092 799 1	0,018 198 9	0,0139 899	0,830 732 1
$u(w_g)$	2,868 7 × 10^{-6}	4,506 5 × 10^{-6}	8,684 × 10^{-6}	3,938 × 10^{-6}	5,947 × 10^{-6}	1,167 × 10^{-5}
V	*n*-Butane	Propane	Ethane	CO_2	N_2	Methane
n-Butane	8,23 × 10^{-12}	–4,02 × 10^{-12}	2,21 × 10^{-12}	5,76 × 10^{-13}	4,42 × 10^{-13}	–7,44 × 10^{-12}
Propane	–4,02 × 10^{-12}	2,03 × 10^{-11}	–1,20 × 10^{-12}	2,13 × 10^{-12}	1,63 × 10^{-12}	–1,88 × 10^{-11}
Ethane	2,21 × 10^{-12}	–1,20 × 10^{-12}	7,54 × 10^{-11}	–4,38 × 10^{-12}	4,00 × 10^{-12}	–7,60 × 10^{-11}
CO_2	5,76 × 10^{-13}	2,13 × 10^{-12}	–4,38 × 10^{-12}	1,55 × 10^{-11}	–1,07 × 10^{-11}	–3,08 × 10^{-12}
N_2	4,42 × 10^{-13}	1,63 × 10^{-12}	4,00 × 10^{-12}	–1,07 × 10^{-11}	3,54 × 10^{-11}	–3,07 × 10^{-11}
Methane	–7,44 × 10^{-12}	–1,88 × 10^{-11}	–7,60 × 10^{-11}	–3,08 × 10^{-12}	–3,07 × 10^{-11}	1,36 × 10^{-10}

6 Inclusion of purity data

The purity data matrix for the gases used for mixture preparation and the corresponding uncertainties are given in Tables 5 and 6 in µmol/mol units.

Table 5 — Purity table for the six gases used in mixture preparation

Values are given in µmol/mol

Content of	*n*-Butane	Propane	Ethane	CO_2	N_2	Methane
Ar					10	
H_2O	10	5	10	5	2	5
N_2		30	20	15	999 983	10
CO				2	1	
CO_2	10	5	5	999 962	1	1
O_2	10	10	10	5	2	5
H_2			5	1	0.5	1
HC	500				0.5	
n-Butane	999 470					
Propane		999 700				
C_3H_6		150				
Ethane			999 745			10
C_2H_4			200			
Methane		100	5	10		999 968

Table 6 — Uncertainties of purity data for the six gases used in mixture preparation

Values are given in µmol/mol

Content of	***n*-Butane**	**Propane**	**Ethane**	CO_2	N_2	**Methane**
Ar	6	3	6	3	1	3
H_2O		5	5	5	3	4
N_2				1	0,5	
CO	6	3	3	9	0,5	0,6
CO_2	6	6	6	3	1	3
O_2			3	0,5	0,3	0,6
H_2	100				0,3	
HC	100					
n-Butane		28				
Propane		25				
C_3H_6			27			6
Ethane			25			
C_2H_4		10	3	6		11
Methane					2	

It can probably be assumed that these purity data were measured independently, i.e. say the CO_2 content in propane does not depend on (and is not correlated with) the CO_2 content in nitrogen or any other of the pure gases. Therefore, correlations between any of the purity data matrix components will not occur.

On the other hand, the governing model equations for the final mixture composition are

$$x_k = \sum_i x_i \cdot x_{i,k}^{\text{pur}} \tag{2}$$

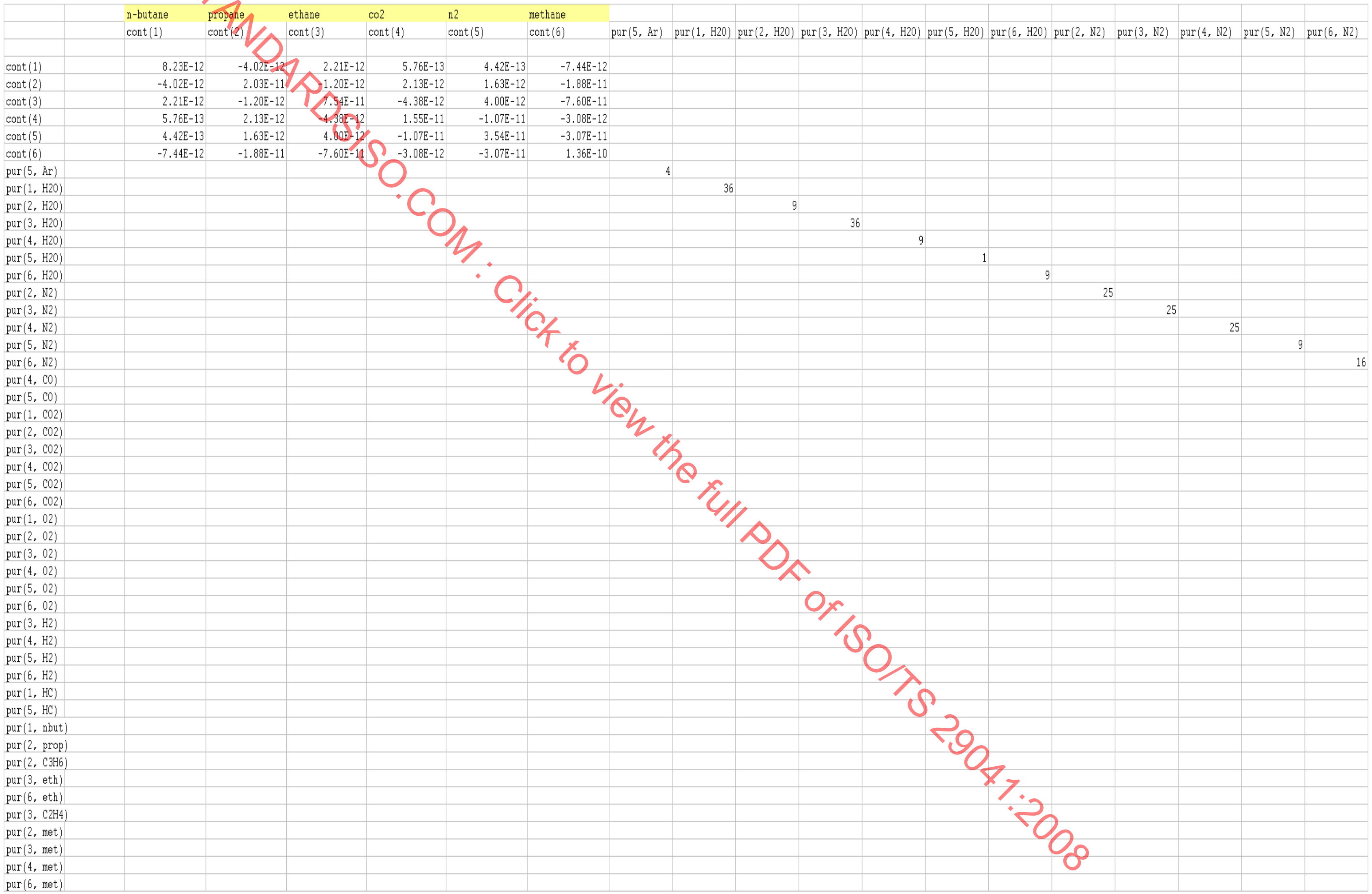
with k running over the 14 different gases contained in the 6 cylinders of “pure” gases used for mixture preparation, and i running over these 6 “pure” gases. The x_i are the “raw” fractions as determined in Clause 3, and the $x_{i,k}^{\text{pur}}$ the purity data from the above table. According to this, one deals with 6 correlated (the x_i) and $6 \times 14 = 84$ uncorrelated (the $x_{i,k}^{\text{pur}}$) input variables which are transformed by the model equation into 14 output variables x_k. Thus, the initial variance-covariance matrix of input variables is a 90×90 matrix. Fortunately, some of the $x_{i,k}^{\text{pur}}$ are equal to zero, and the rows and columns corresponding to these $x_{i,k}^{\text{pur}}$ may be deleted from the input variable variance-covariance matrix. After deleting zero rows and columns, there is still a 48×48 matrix to deal with. The left part of the matrix containing the 6×6 correlated gas composition data and 12 uncertainties of the $x_{i,k}^{\text{pur}}$ is shown in Figure 1.

Note that due to its dimensions:

a) only the upper left part of the matrix is shown; and

b) this part is reproduced in a graphics mode.

The matrix continues further to the right but is strictly diagonal in this part.



		n-butane	propane	ethane	co2	n2	methane												
		cont(1)	cont(2)	cont(3)	cont(4)	cont(5)	cont(6)	pur(5, Ar)	pur(1, H2O)	pur(2, H2O)	pur(3, H2O)	pur(4, H2O)	pur(5, H2O)	pur(6, H2O)	pur(2, N2)	pur(3, N2)	pur(4, N2)	pur(5, N2)	pur(6, N2)
cont(1)		8.23E-12	-4.02E-12	2.21E-12	5.76E-13	4.42E-13	-7.44E-12												
cont(2)		-4.02E-12	2.03E-11	-1.20E-12	2.13E-12	1.63E-12	-1.88E-11												
cont(3)		2.21E-12	-1.20E-12	7.54E-11	-4.38E-12	4.00E-12	-7.60E-11												
cont(4)		5.76E-13	2.13E-12	-4.38E-12	1.55E-11	-1.07E-11	-3.08E-12												
cont(5)		4.42E-13	1.63E-12	4.00E-12	-1.07E-11	3.54E-11	-3.07E-11												
cont(6)		-7.44E-12	-1.88E-11	-7.60E-11	-3.08E-12	-3.07E-11	1.36E-10												
pur(5, Ar)								4											
pur(1, H2O)									36										
pur(2, H2O)										9									
pur(3, H2O)											36								
pur(4, H2O)												9							
pur(5, H2O)													1						
pur(6, H2O)														9					
pur(2, N2)															25				
pur(3, N2)																25			
pur(4, N2)																	25		
pur(5, N2)																		9	
pur(6, N2)																			16
pur(4, CO)																			
pur(5, CO)																			
pur(1, CO2)																			
pur(2, CO2)																			
pur(3, CO2)																			
pur(4, CO2)																			
pur(5, CO2)																			
pur(6, CO2)																			
pur(1, O2)																			
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pur(5, H2)																			
pur(6, H2)																			
pur(1, HC)																			
pur(5, HC)																			
pur(1, nbut)																			
pur(2, prop)																			
pur(2, C3H6)																			
pur(3, eth)																			
pur(6, eth)																			
pur(3, C2H4)																			
pur(2, met)																			
pur(3, met)																			
pur(4, met)																			
pur(6, met)																			

NOTE The letter “E” is used for “times ten raised to the power”. The decimal point is shown in this screen capture instead of the decimal comma used in the rest of the text.

Figure 1 — Variance-covariance for the purity data of the gases used for mixture composition

From the model equation as above, the final molar fractions of the 14 gas components and the transfer matrix $\boldsymbol{Q}$ are determined. Using the latter, then the variance-covariance matrix for the 14 gas components is calculated. This yields for the composition of the mixture (in µmol/mol) as in Table 7 and the variance-covariance matrix as given in Figure 2 (matrix is displayed also in graphics mode, unit is (µmol/mol^2).

Table 7 — Final molar fractions for the 14 gases in the mixture

Gas component	**Content** µmol/mol	***u* (content)** µmol/mol
Ar	0,140	0,028
H_2O	5,472	2,557
N_2	14 001,168	6,831
CO	0,050	0,019
CO_2	18 199,778	3,984
O_2	5,643	2,563
H_2	1,320	0,571
HC	4,993	0,997
n-Butane	9 966,352	3,036
Propane	34 297,998	4,606
C_3H_6	5,146	0,858
Ethane	92 783,754	10,320
C_2H_4	18,560	2,320
Methane	830 709,593	14,826

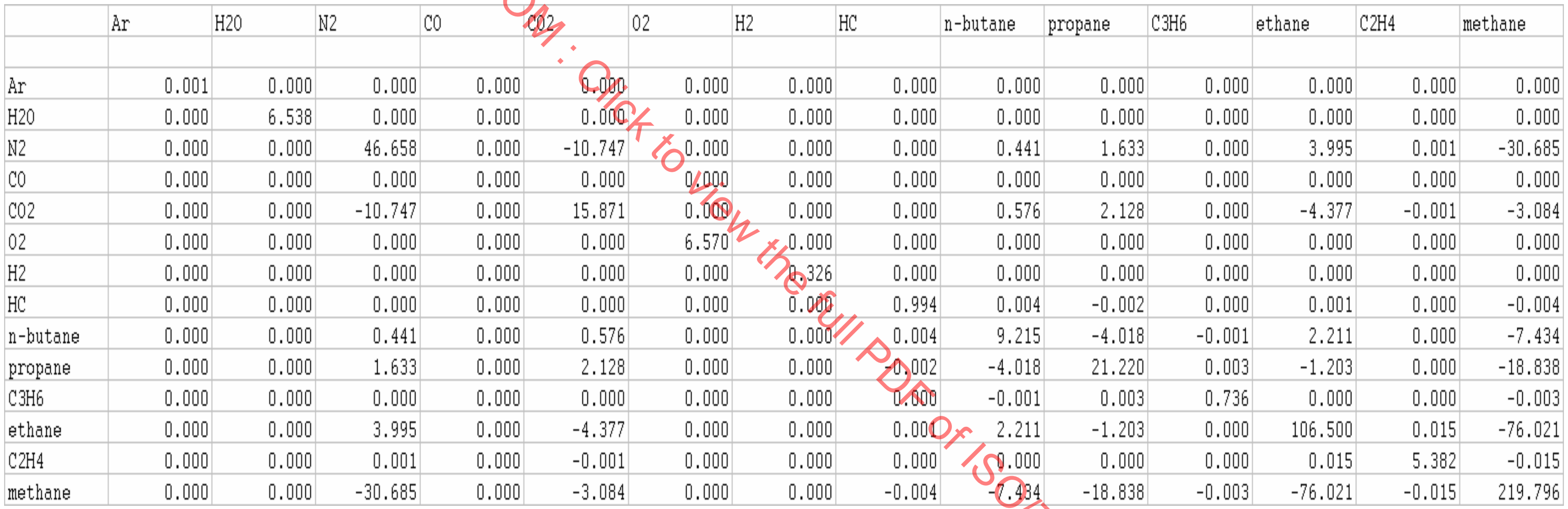
7 Gas property calculation

From the final composition given in Table 7 above, gas properties can be calculated using the model equations and pure gas property values given in ISO 6976 [3]. It may be preferable first to calculate the CV on a molar basis, and the molar mass of the mixture. Both values depend on the gas composition (and are thus correlated) and the properties of the pure gases. The latter are (still) given without uncertainties in ISO 6976, so they can be considered as parameters. The problem has 14 input and 2 output variables, and with the transfer matrix calculated from the model Equations (3) and (4),

$$\mathrm{CV} = \sum_i x_i \cdot \mathrm{CV}_i \tag{3}$$

$$M = \sum_i x_i \cdot M_i \tag{4}$$

the results given in Table 8 are obtained.



	Ar	H2O	N2	CO	CO2	O2	H2	HC	n-butane	propane	C3H6	ethane	C2H4	methane
Ar	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2O	0.000	6.538	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N2	0.000	0.000	46.658	0.000	-10.747	0.000	0.000	0.000	0.441	1.633	0.000	3.995	0.001	-30.685
CO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
CO2	0.000	0.000	-10.747	0.000	15.871	0.000	0.000	0.000	0.576	2.128	0.000	-4.377	-0.001	-3.084
O2	0.000	0.000	0.000	0.000	0.000	6.570	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H2	0.000	0.000	0.000	0.000	0.000	0.000	0.326	0.000	0.000	0.000	0.000	0.000	0.000	0.000
HC	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.994	0.004	-0.002	0.000	0.001	0.000	-0.004
n-butane	0.000	0.000	0.441	0.000	0.576	0.000	0.000	0.004	9.215	-4.018	-0.001	2.211	0.000	-7.434
propane	0.000	0.000	1.633	0.000	2.128	0.000	0.000	-0.002	-4.018	21.220	0.003	-1.203	0.000	-18.838
C3H6	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001	0.003	0.736	0.000	0.000	-0.003
ethane	0.000	0.000	3.995	0.000	-4.377	0.000	0.000	0.001	2.211	-1.203	0.000	106.500	0.015	-76.021
C2H4	0.000	0.000	0.001	0.000	-0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.015	5.382	-0.015
methane	0.000	0.000	-30.685	0.000	-3.084	0.000	0.000	-0.004	-7.434	-18.838	-0.003	-76.021	-0.015	219.796

NOTE The decimal point is shown in this screen capture instead of the decimal comma used in the rest of the text.

Figure 2 — Variance-covariance matrix of the final mixture composition data unit is (μmol/mol^2)

Table 8 — Calorific value and molar mass of the gas mixture

Value [unit [a]]	**Value**	*u*(**value**) **correlation**	*U*(**value**) **without correlation**
CV on a molar basis [kJ/mol]	990,503 8	0,016 7	0,025 3
CV on mass basis [MJ/kg]	51,048 0	0,000 6	0,001 3
CV on volume basis [MJ/m^3]	41,890 2	0,000 7	0,001 1
Molar mass [kg/mol]	19,403 4	0,000 4	0,000 6

[a] kJ/mol = 10^3 kg·m^2 mol^{-1} s^{-2}; MJ/kg = 10^6 m^2 mol^{-1} s^{-2}; MJ/m^3 = 10^6 kg m^{-1} mol^{-1} s^{-2}.

Results are given for

a) the case where correlations are fully taken into account, and

b) the case where correlations are neglected (for comparison reasons).

It is obvious that correlations have a certain and significant impact on the uncertainties of the final results. Here, result uncertainties are considerably reduced. From the CV on a molar basis and the molar mass of the mixture, the CV on a mass basis can be calculated and, finally, also the CV on a volumetric basis. According to ISO 6976, the latter is a transformation of the CV on a molar basis using a transformation coefficient calculated from state conditions. Consequently, the CV on a molar basis and its uncertainty are only scaled by a corresponding scaling factor, no additional correlation must be taken into account.

8 Summary and recommendations

Two major conclusions can obviously be drawn from the above.

1) Correlations have a certain and significant impact on the uncertainties of the final results. Resulting uncertainties are considerably reduced in the example discussed here. Speciality gas producers and suppliers, claiming high-level accuracy or product applications in the field of establishment and dissemination of metrological traceability, are recommended to fully account for correlations and include them in uncertainty budgets. Whether a reduction by a factor of 1,5 to 2,2 of an uncertainty, which is already in the region of 10^{-5} to 10^{-4} (relative), really matters with respect to the intended use of the gas mixtures ("fit-for-purpose" considerations) shall only be decided for each and every particular case, and may be challenged.

2) The calculatory efforts considerably increase when correlations are taken into account. This additional effort should not be justified in all cases. In particular, it seems problematic to recommend accounting for correlations in commercial environments where speciality gases are produced as stand-alone items tailored with respect to the needs of each individual customer. On the other hand, in the cases where pre-defined product lines are fabricated in larger batches, and (more or less) fixed SOPs are followed, uncertainty budget calculations including covariances may be both justifiable and feasible.

Annex A
(normative)

Generic approach to uncertainty calculation

A.1 Introduction

In accordance with basic guidelines to the expression of measurement uncertainty, namely the GUM [4] and the EURACHEM Guide [5], the procedure can be sub-divided into the following four basic steps:

1) definition/specification of the measurand;

2) identification of uncertainty sources;

3) quantification of uncertainty contributions;

4) calculation of the combined standard uncertainty.

This annex will not deal with step 3, the quantification of uncertainty contributions, since this is described elsewhere in full detail, and methods for generating sensible uncertainty estimates may vary not only between different methods and applications, but also from implementation to implementation in different laboratories. All other steps are described below.

A.2 Definition of the measurand

Throughout this annex, definition of the measurand is meant in a more metrological sense and refers to the establishment of operational relationships, a correct specification of the measurand (e.g. the establishment of conditions under which a specific compound is extracted from a matrix or separated from other compounds, or the attribution of a chromatographic peak to a specific compound) is assumed. Definition of the measurand includes the (formal) definition of what are the output variables of an analytical procedure or a calculation, the definition of all input variables which the output variables depend on, and the establishment of a suitable relationship describing how the output variables depend on the input variables, i.e. the model. This model may be deduced from physical or chemical laws or may reflect empirically established relationships, and it may appear in the form of a single equation, a series of equations which describe, e.g. intermediate results and are applied consecutively, a system of equations, or even a network of modules each of which consists of one or several equations and may even include purely numerical procedures (i.e. iterative algorithms reflected in a computer programme).

Let the vector $\boldsymbol{z} = (z_1, ..., z_k)^\mathrm{T}$ be the vector of the k output variables, and $\boldsymbol{p} = (p_1, ..., p_n)^\mathrm{T}$ the vector of the n input variables which the output variables depend on. The model describes the relationship between output and input variables via a system of equations $\boldsymbol{G}$ such that, in the most general case, it holds

$$\boldsymbol{G}(\boldsymbol{z}, \boldsymbol{p}) = 0 \qquad \text{(A.1)}$$