TECHNICAL SPECIFICATION

ISO/TS 29041

First edition
2008-02-01

Gas mixtures — Gravimetric preparation — Mastering correlations in composition

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

Reference number
ISO/TS 29041:2008(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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
$u(m_m)$ [mg]	0,015	0,019 3	0,010 8	0,015	0,020 2	0,015 1	0,06
$u(u_m)$ [mg]	2,3	2,3	2,3	2,3	2,3	2,3	2,3
$u(u_B)$ [mg]	0,019	0,014	0,003	0,019	0,025	0,028	0,13
$u(u_{exp})$ [mg]					0,86		9,16
$u(u_R)$ [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

$$u^2(m_x) = u^2(m_m) + u^2(u_m) + u^2(u_B) \quad (1)$$

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 $u^2(m_m)$ of the initial weighing of the mixture cylinder containing only vacuum [$u(m_m) = 0{,}015$ mg, $u^2(m_m) = 0{,}000\ 225$ 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:

$$m_g(\text{butane}) - m_{vac} + m_{butane} = 0$$

$$m_g(\text{propane}) - m_{butane} + m_{propane} = 0$$

$$m_g(\text{ethane}) - m_{propane} - m_{ethane} = 0$$

$$m_g(CO_2) - m_{CO2} + m_{ethane} = 0$$

$$m_g(N_2) - m_{N2} + m_{CO2} = 0$$

$$m_g(\text{methane}) - m_{methane} + m_{N2} = 0$$

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
$u(m_g)$ [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
$u(w_g)$	$2{,}868\,7 \times 10^{-6}$	$4{,}506\,5 \times 10^{-6}$	$8{,}684 \times 10^{-6}$	$3{,}938 \times 10^{-6}$	$5{,}947 \times 10^{-6}$	$1{,}167 \times 10^{-5}$
V	*n*-Butane	Propane	Ethane	CO_2	N_2	Methane
n-Butane	$8{,}23 \times 10^{-12}$	$-4{,}02 \times 10^{-12}$	$2{,}21 \times 10^{-12}$	$5{,}76 \times 10^{-13}$	$4{,}42 \times 10^{-13}$	$-7{,}44 \times 10^{-12}$
Propane	$-4{,}02 \times 10^{-12}$	$2{,}03 \times 10^{-11}$	$-1{,}20 \times 10^{-12}$	$2{,}13 \times 10^{-12}$	$1{,}63 \times 10^{-12}$	$-1{,}88 \times 10^{-11}$
Ethane	$2{,}21 \times 10^{-12}$	$-1{,}20 \times 10^{-12}$	$7{,}54 \times 10^{-11}$	$-4{,}38 \times 10^{-12}$	$4{,}00 \times 10^{-12}$	$-7{,}60 \times 10^{-11}$
CO_2	$5{,}76 \times 10^{-13}$	$2{,}13 \times 10^{-12}$	$-4{,}38 \times 10^{-12}$	$1{,}55 \times 10^{-11}$	$-1{,}07 \times 10^{-11}$	$-3{,}08 \times 10^{-12}$
N_2	$4{,}42 \times 10^{-13}$	$1{,}63 \times 10^{-12}$	$4{,}00 \times 10^{-12}$	$-1{,}07 \times 10^{-11}$	$3{,}54 \times 10^{-11}$	$-3{,}07 \times 10^{-11}$
Methane	$-7{,}44 \times 10^{-12}$	$-1{,}88 \times 10^{-11}$	$-7{,}60 \times 10^{-11}$	$-3{,}08 \times 10^{-12}$	$-3{,}07 \times 10^{-11}$	$1{,}36 \times 10^{-10}$

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