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Natural gas — Determination of composition and associated uncertainty by gas chromatography —

Part 3: Precision and bias

Gaz naturel — Détermination de la composition et de l'incertitude associée par chromatographie en phase gazeuse —

Partie 3: Fidélité et biais

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas.*

This second edition cancels and replaces the first edition (ISO 6974-3:2000), which has been technically revised.

A list of all parts in the ISO 6974 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Natural gas — Determination of composition and associated uncertainty by gas chromatography —

Part 3: Precision and bias

1 Scope

This document describes the precision that can be expected from the gas chromatographic method that is set up in accordance with ISO 6974-1. The stated precision provides values for the magnitude of variability that can be expected between test results when the method described in ISO 6974-1 is applied in one or more competent laboratories. This document also gives guidance on the assessment of bias.

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 17025, *General requirements for the competence of testing and calibration laboratories*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at: http://www.electropedia.org/

3.1
measurement precision
closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

Note 1 to entry: Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.

Note 2 to entry: The 'specified conditions' can be, for example, repeatability conditions of measurement, intermediate precision conditions of measurement, or reproducibility conditions of measurement (see ISO 5725-1).

Note 3 to entry: Measurement precision is used to define measurement repeatability, intermediate measurement precision, and measurement reproducibility.

Note 4 to entry: Sometimes "measurement precision" is erroneously used to mean measurement accuracy.

[SOURCE: JCGM 200:2012, 2.15]

3.2
error of measurement
measured quantity value minus a reference quantity value

Note 1 to entry: The concept of 'measurement error' can be used both

a) when there is a single reference quantity value to refer to, which occurs if a calibration is made by means of a measurement standard with a measured quantity value having a negligible measurement uncertainty or if a conventional quantity value is given, in which case the measurement error is known, and

b) if a measurand is supposed to be represented by a unique true quantity value of a set of true quantity values of negligible range in which case the measurement error is not known

Note 2 to entry: Measurement error should not be confused with production error or mistake.

[SOURCE: JCGM 200:2012, 2.16]

3.3
systematic measurement error
component of measurement error that in replicate measurements remains constant or varies in a predictable manner

Note 1 to entry: A reference quantity value for a systematic measurement error is a true quantity value, or a measured quantity value of a measurement standard of negligible measurement uncertainty, or a conventional quantity value.

Note 2 to entry: Systematic measurement error, and its causes, can be known or unknown. A correction can be applied to compensate for a known systematic measurement error.

Note 3 to entry: Systematic measurement error equals measurement error minus random measurement error.

[SOURCE: JCGM 200:2012, 2.17]

3.4
measurement bias
estimate of a systematic measurement error

[SOURCE: JCGM 200:2012, 2.18]

3.5
laboratory bias
difference between the expectation of the test results from a particular laboratory and an accepted reference value

[SOURCE: ISO 5725-1:1994, 3.9]

3.6
random measurement error
component of measurement error that in replicate measurements varies in an unpredictable manner

Note 1 to entry: A reference quantity value for a random measurement error is the average that would ensue from an infinite number of replicate measurements of the same measurand.

Note 2 to entry: Random measurement errors of a set of replicate measurements form a distribution that can be summarized by its expectation, which is generally assumed to be zero, and its variance.

Note 3 to entry: Random measurement error equals measurement error minus systematic measurement error.

[SOURCE: JCGM 200:2012, 2.19]

3.7
repeatability condition of measurement
condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

Note 1 to entry: A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

Note 2 to entry: In chemistry, the term "intra-serial precision condition of measurement" is sometimes used to designate this concept.

[SOURCE: JCGM 200:2012, 2.20]

3.8
measurement repeatability
measurement precision under a set of repeatability conditions of measurement

[SOURCE: JCGM 200:2012, 2.21]

3.9
reproducibility condition of measurement
condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

Note 1 to entry: The different measuring systems may use different measurement procedures.

Note 2 to entry: A specification should give the conditions changed and unchanged, to the extent practical.

[SOURCE: JCGM 200:2012, 2.20]

Note 3 to entry: Where repeatability is related to replicate measurements over a short period of time, reproducibility is related to replicate measurements over a longer period of time.

3.10
measurement reproducibility
measurement precision under reproducibility conditions of measurement

Note 1 to entry: Relevant statistical terms are given in ISO 5725-1 and ISO 5725-2.

[SOURCE: JCGM 200:2012, 2.25]

3.11
assigned value
value attributed to a particular property of a proficiency test item

[SOURCE: ISO 17043:2010, 3.1]

3.12
repeatability standard deviation
s_r
standard deviation of test results obtained under repeatability conditions

Note 1 to entry: It is a measure of dispersion of the distribution of test results under repeatability conditions.

Note 2 to entry: Similarly "repeatability variance" and "repeatability coefficient of variation" could be defined and used as measures of the dispersion of test results under repeatability conditions.

[SOURCE: ISO 5725-1:1994, 3.15]

3.13
reproducibility standard deviation
s_R
standard deviation of test results obtained under reproducibility conditions

Note 1 to entry: It is a measure of dispersion of the distribution of test results under reproducibility conditions.

Note 2 to entry: Similarly "reproducibility variance" and "reproducibility coefficient of variation" could be defined and used as measures of the dispersion of test results under reproducibility conditions.

[SOURCE: ISO 5725-1:1994, 3.19]

4 Symbols

s	standard deviation
s_r	repeatability standard deviation
s_R	reproducibility standard deviation
x_i	amount of substance fraction of component i in the natural gas mixture

5 Principle

The precision data that can be expected from the gas chromatographic method that is set up in accordance with ISO 6974-1, are based on the statistical evaluation of data from 14 individual Proficiency Testing (PT) exercises that have been organized from 2012 to 2014. The precision is expressed as repeatability and reproducibility.

The scope and component ranges of these PT schemes is given in Table 1.

Table 1 — Scope of Proficiency Testing Schemes

	Mole fraction %	
	PT Provider #1	PT Provider #2
Ethane	0,1 to 14	3 to 9
Propane	0,05 to 5	2 to 5
i-Butane	0,01 to 1	0,1 to 1
n-Butane	0,01 to 1	0,1 to 1
i-Pentane	0,005 to 0,35	0,02 to 0,5
n-Pentane	0,005 to 0,35	0,02 to 0,5
Hexane	0,001 to 0,35	0,01 to 0,1
Nitrogen	0,1 to 8	0,1 to 8
CO_2	0,1 to 8	0,1 to 8
Methane	balance	65 to 99

Details on the actual data processing can be found in informative Annex A.

6 Reference precision values

Repeatability and reproducibility standard deviations, s_r and s_R respectively, are derived from the PT data. Non-methane components are treated as a group; methane is treated separately.

For methane the repeatability standard deviation of normalized results is 0,038 % relative and the reproducibility standard deviation of normalized results is 0,09 % relative.

For all non-methane components, the repeatability standard deviation of normalized results is given by the relationship:

$$\ln(s_r) = -5{,}64 + 0{,}58 \times \ln(x_i) \quad (1)$$

And the reproducibility standard deviation of normalized results is given by the relationship:

$$\ln(s_R) = -4{,}28 + 0{,}715 \times \ln(x_i) \quad (2)$$

Typical precision values are given in Table 2 and Table 3.

Table 2 — Precision of measurement results for selected methane mole fractions

x_i %	s_r % Absolute	s_R % Absolute
75	0,028	0,07
95	0,036	0,09

Table 3 — Precision of measurement results for selected mole fractions for non-methane components

x_i %	s_r % Absolute	s_R % Absolute
0,01	0,000 25	0,000 5
0,1	0,000 93	0,002 7
1	0,003 6	0,014
10	0,014	0,072

7 Practical applications

The standard deviation from repeated injections under repeatability conditions can be compared to the repeatability standard deviation as given for methane or as calculated with Formula (1) to evaluate correct implementation of the method. It can also be used during an acceptance test for newly built equipment to evaluate performance.

The standard deviation values given in Clause 6 are derived from normalised mole fraction data. Similar data shall be used for calculating precision values to be compared with those given in Clause 6. The number of repeat measurements made to achieve a valid comparison is ten. If this is not possible a minimum of five measurements can be used, but the comparison will be statistically less significant. It is also important that any testing for precision follows the normal procedures used at site. So if in normal practice the data from the first injection are rejected, the laboratory should do the same for their own test data. For reproducibility it is important to check the data set for normal distribution (for example Anderson-Darling statistic[5]).

Laboratories can evaluate laboratory precision using Statistical Quality Control. Periodic injection of a Working Measurement Standard over a longer period of time, as described in ISO 6974-1 can be used to estimate the site precision. The value for this laboratory precision should be compared to the value for s_R as calculated using Formula (2) for non-methane components and given for methane. For this comparison a chi-squared test should be used to test if the differences between the observed laboratory precision and the reference values given in Clause 6 are significant from a statistical point of view.

8 Bias

The bias of a measurement process is a consistent or systematic difference between an average of a set of test results and the assigned value for the measured property.

Therefore, when an assigned value is not available, the bias cannot be established.

Test method variability includes systematic as well as random components. The systematic components can be evaluated if a certified reference material with a certified value of the components content being measured is available. The average value of a series of repeated measurements minus the certified value is an estimate of the bias. The standard deviation in repeated measurements gives an estimate of the random components and can be evaluated against the repeatability standard deviation given in this document.

Another acceptable way of bias control is frequent participation in a PT exercise with an assigned value.

Bias arising from non-linearity error is described in ISO 6974-1.

Annex A
(informative)

Proficiency scheme data evaluation

The characteristics of the PT exercises are:

— The number of participants submitting independent results was on average 17;

— Participation was from around the world by experienced laboratories;

— Participants are laboratories active in (liquefied) natural gas analysis;

— The majority of participants shall have an accredited quality system in accordance with ISO/IEC 17025;

— Data was evaluated against an assigned value;

— The assigned value was for all constituents a reference value as determined by comparison of the proficiency test item alongside a reference material or standard, traceable to a national or international standard (see ISO 17043:2010, B.2.1 option c);

— Participants all used chromatography as measurement technique; no distinction between the actual designs of the gas chromatograph (GC) was made.

The results in the PT exercises are not classified against a specific GC configuration. The repeatability of the GC is in general not depending on the specific column configuration.

The data are treated analogous to the procedures described in ISO 5725-1 and ISO 5725-2. First, from the complete set of the reported data the grand mean, $\hat{m}$, the repeatability standard deviation, s_r, the between-laboratory standard deviation, s_L, and the reproducibility standard deviation, s_R, are calculated.

The consensus value is defined according to:

$$\hat{m} = \bar{y} = \frac{\sum_{i=1}^{p} n_i \bar{y}_i}{\sum_{i=1}^{p} n_i} \tag{A.1}$$

where n_i equals the number of results reported by laboratory i, $\bar{y}_i$ the average result of this laboratory and p is the total number of laboratories. The repeatability standard deviation follows from:

$$s_r^2 = \frac{\sum_{i=1}^{p} (n_i - 1) s_i^2}{\sum_{i=1}^{p} (n_i - 1)} \tag{A.2}$$

where s_i is the repeatability standard deviation of the results of laboratory i.

The between-laboratory standard deviation is calculated according to:

$$s_L^2 = \frac{s_d^2 - s_r^2}{\overline{\overline{n}}} \tag{A.3}$$

where

$$s_d^2 = \frac{1}{p-1}\sum_{i=1}^{p} n_i \left(\overline{y_i} - \overline{\overline{y}}\right)^2 \tag{A.4}$$

$\overline{\overline{n}}$ is defined as

$$\overline{\overline{n}} = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i}\right] \tag{A.5}$$

The reproducibility standard deviation is calculated according to:

$$s_R^2 = s_L^2 + s_r^2 \tag{A.6}$$

The complete data set is also used to calculate a number of robust estimates: the median (y_{med}), the median of absolute differences (MAD) and the average absolute deviation (AAD).

The absolute differences are calculated according to:

$$d_i = \left|\overline{y}_i - y_{\text{med}}\right| \tag{A.7}$$

and the average absolute deviation according to:

$$AAD = \frac{1}{p}\sum_{i=1}^{p} d_i \tag{A.8}$$

The procedure for checking on outliers is different from the methods described in ISO 5725-2. Outliers are defined as follows. A raw z-score is calculated from the laboratory averages, the median and *MAD*, according to:

$$z_{\text{raw},i} = \frac{\overline{y}_i - y_{\text{med}}}{1{,}482\,6 \times MAD} \tag{A.9}$$

where 1,482 6 is the value for the constant scale factor K assuming normal distribution.

In case $|z_{\text{raw},i}| \geq 3$, the result concerned ($\overline{y}_i$) is removed from the data set.

In Figure A.1 the repeatability and in Figure A.2 the reproducibility data are plotted for all 10 constituents together with the resulting regression line. Methane values are not included in the regression.