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Natural gas — Performance evaluation for analytical systems

Gaz naturel — Évaluation des performances des systèmes d'analyse

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10723 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 10723:1995), which has been technically revised. It also incorporates Technical Corrigendum ISO 10723:1995/Cor.1:1998.

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Introduction

This International Standard describes a method for evaluating the performance of analytical systems intended for the analysis of natural gas. Natural gas is assumed to consist predominantly of methane, with other saturated hydrocarbons and non-combustible gases.

Performance evaluation makes no assumption about equipment for and/or methodology of analysis but gives test methods which can be applied to the chosen analytical system, including the method, equipment and sample handling.

This International Standard contains an informative annex (Annex A) that shows the application for an on-line gas chromatographic system which, as described, is assumed to have a response/concentration relationship for all components that is represented by a straight line through the origin. This International Standard contains an additional informative annex (Annex B) that gives a rationale for the approach used for instrument benchmarking.

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Natural gas — Performance evaluation for analytical systems

1 Scope

1.1   This International Standard specifies a method of determining whether an analytical system for natural gas analysis is fit for purpose. It can be used either

a)   to determine a range of gas compositions to which the method can be applied, using a specified calibration gas, while satisfying previously defined criteria for the maximum errors and uncertainties on the composition or property or both, or

b)   to evaluate the range of errors and uncertainties on the composition or property (calculable from composition) or both when analysing gases within a defined range of composition, using a specified calibration gas.

1.2   It is assumed that

a)   for evaluations of the first type above, the analytical requirement has been clearly and unambiguously defined, in terms of the range of acceptable uncertainty on the composition, and, where appropriate, the uncertainty in physical properties calculated from these measurements,

b)   for applications of the second type above, the analytical requirement has been clearly and unambiguously defined, in terms of the range of composition to be measured and, where appropriate, the range of properties which may be calculated from these measurements,

c)   the analytical and calibration procedures have been fully described, and

d)   the analytical system is intended to be applied to gases having compositions which vary over ranges normally found in gas transmission and distribution systems.

1.3   If the performance evaluation shows the system to be unsatisfactory in terms of the uncertainty on the component amount fraction or property, or shows limitations in the ranges of composition or property values measurable within the required uncertainty, then it is intended that the operating parameters, including

a)   the analytical requirement,

b)   the analytical procedure,

c)   the choice of equipment,

d)   the choice of calibration gas mixture, and

e)   the calculation procedure,

be reviewed to assess where improvements can be obtained. Of these parameters, the choice of the calibration gas composition is likely to have the most significant influence.

1.4   This International Standard is applicable to analytical systems which measure individual component amount fractions. For an application such as calorific value determination, the method will be typically gas chromatography, set up, as a minimum, for the measurement of nitrogen, carbon dioxide, individual hydrocarbons from C_1 to C_5 and a composite measurement representing all higher hydrocarbons of carbon number 6 and above. This allows for the calculation of calorific value and similar properties with acceptable accuracy. In addition, components such as H_2S can be measured individually by specific measurement methods to which this evaluation approach can also be applied.

1.5 Performance evaluation of an analytical system is intended to be performed following initial installation to ensure that errors associated with assumed response functions are fit for purpose. Thereafter, periodic performance evaluation is recommended, or whenever any critical component of the analytical system is adjusted or replaced. The appropriate interval between periodic performance evaluations will depend upon both how instrument responses vary with time and also how large an error may be tolerated. This first consideration is dependent upon instrument/operation; the second is dependent on the application. It is not appropriate, therefore, for this International Standard to offer specific recommendations on intervals between performance evaluations.

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/IEC Guide 98-3:2008, *Uncertainty of measurement —Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO 6143:2001, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6974-2, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

ISO 6976:1995, *Natural gas — Calculation of calorific values, density, relative density and Wobbe index from composition*

3 Terms and definitions

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

3.1
uncertainty of measurement
parameter, associated with the result of a measurement, that characterizes the dispersion of values that can reasonably be attributed to the measurand

NOTE   In keeping with ISO/IEC Guide 98-3, in this International Standard the uncertainty of the composition is expressed as a standard uncertainty or as an expanded uncertainty calculated through the use of an appropriate coverage factor.

3.2
certified reference gas mixture
CRM
reference gas mixture, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

NOTE 1   The above definition is based on the definition of "certified reference material" in ISO Guide 35[3]. "Certified reference material" is a generic term; "certified reference gas mixture" is more suited to this application.

NOTE 2   Metrologically valid procedures for the production and certification of reference materials (such as certified reference gas mixtures) are given in, among others, ISO Guide 34[4] and ISO Guide 35[3].

NOTE 3   ISO Guide 31[5] gives guidance on the contents of certificates.

3.3
working measurement standard
WMS
standard that is used routinely to calibrate or verify measuring instruments or measuring systems

[ISO/IEC Guide 99:2007, 5.7]

NOTE   A working measurement standard is usually calibrated against a CRM.

3.4
calibration gas mixture
CGM
gas mixture whose composition is sufficiently well established and stable to be used as a working measurement standard of composition

NOTE   In this International Standard, a CGM is used for routine (e.g. daily) component calibration of the analyser. It is independent of the WMSs used to perform the evaluation.

3.5
response
output signal of the measuring system for each specified component

NOTE   In the case of gas chromatography this will be either peak area or peak height, depending upon the instrument configuration.

3.6
response function
functional relationship between instrumental response and component content

NOTE 1   The response function can be expressed in two different ways as a calibration function or an analysis function, depending on the choice of the dependent and the independent variable.

NOTE 2   The response function is conceptual and cannot be determined exactly. It is determined approximately through calibration.

3.7
calibration function
relationship describing instrument response as a function of component content

3.8
analysis function
relationship describing component content as a function of instrument response

4   Symbols

a_z parameters of the calibration function (z = 0, 1, 2 or 3)

b_z parameters of the analysis function (z = 0, 1, 2 or 3)

x amount fraction of the specified component

$\hat{x}$ adjusted (estimated) amount fraction from the response function

y' raw instrumental response

y corrected instrumental response

s standard deviation of response

$\hat{y}$ adjusted (estimated) response from the response function

F	calibration function
G	analysis function
M	(sample of) reference gas mixture
P	general characteristic (physical property)
p	pressure (in kPa)
u	standard uncertainty
U	expanded uncertainty
k	coverage factor
Γ	goodness-of-fit measure in generalized least squares
δ	error in the estimated value

5 Principle

Performance characteristics of the instrument are determined when used in combination with a specified calibration gas mixture. Therefore, the evaluation procedure can be used to

— determine errors and uncertainties in measured composition and properties over a pre-defined range for each specified component, and

— determine a range for each specified component over which the errors and uncertainties in measured composition and properties do not exceed a predefined measurement requirement.

In each case, the performance characteristics are calculated for the instrument when used in combination with a specified calibration gas mixture of known composition and uncertainty.

NOTE 1   The method can also be used to establish the most appropriate composition of the calibration gas mixture to be used routinely with the instrument such that the errors and uncertainties are minimized over a predefined range of use.

A complete assessment of the errors and uncertainties arising from the use of an instrument could be performed by measuring an infinite series of well-defined reference gas mixtures whose compositions lie within the specified range of operation. However, this is practically impossible. Instead, the principle used in this International Standard is to measure a smaller number of well-defined reference gases and to determine a mathematical description of the response functions for each specified component over a predefined content range. The performance of the instrument can then be modelled offline using these "*true*" response functions, the response functions *assumed* by the instrument's data system and the reference data for the calibration gas mixture specified for the instrument. The measurement of a large number of gas mixtures can then be simulated offline using numerical methods to determine performance benchmarks inherent in the measurement system.

The general procedure for determining the performance characteristics of the instrument is summarized below.

a) Specify the components required to be measured by the instrument and the range for each over which the instrument shall be evaluated.

b) Establish the functional descriptions of the response functions assumed by the instrument (or the instrument's data system) for each specified component.

NOTE 2   These functions are referred to as the *assumed* response functions of the system at the time of calibration/evaluation. These are generally analysis functions used by the instrument to determine the amount from the measured response, $x = G_{asm}(y)$.

c) Establish the composition and uncertainty of the calibration gas mixture specified for routine calibration of the instrument.

d) Design a set of reference gas mixtures with compositions covering all ranges for all components specified in a).

e) Perform a multi-point calibration experiment by collecting instrument response data to measurements of the reference gas mixtures designed and produced in accordance with d). The entire experiment should be conducted within a time period equivalent to that between routine calibrations.

f) Calculate the calibration functions and analysis functions for each specified component using regression analysis and validate the compatibility of the functions with the calibration data set.

NOTE 3   These functions are referred to as the *true* response functions of the system at the time of calibration/evaluation, $y = F_{true}(x)$ and $x = G_{true}(y)$.

g) Calculate instrumental errors and uncertainties for each component and property over a specified range of compositions using the functions and reference data collated in d), e) and f) above.

h) From the distribution of errors and the unbiased uncertainty estimates calculated in g) above, determine the mean error and its uncertainty for each measurand.

The mean errors and their uncertainties on component content and properties resulting from step h) can be compared to performance requirements for the analytical system. If performance benchmarks are poorer than the analytical requirements of the measurement, then it is clear that the method fails to provide the desired performance over the fully specified range. The method shall be modified accordingly and the entire evaluation procedure repeated. Alternatively, the offline calculations shall be repeated over a restricted range of operation in order to improve system performance. In this case, the instrument may be shown to perform adequately over a limited range.

It may be possible to modify the data system on the instrument to allow for the difference between the true response functions and the analysis function assumed by the instrument. In this case, the instrument should be adjusted following the evaluation to account for this difference. If the function form of G_{true} and G_{asm} are the same, then the parameters of G_{asm} in the instrument's data system can be updated with those determined for G_{true} in step f) above, thereby eliminating systematic errors due to the instrument. However, it is important to remember that the parameters of G_{true} are only valid for each component over the content range used to establish the analysis function. That is, the instrument should not be used outside the ranges defined, designed and evaluated in steps a), b) and c).

6   General procedure

6.1   Analytical requirements

6.1.1   General considerations

Users of this International Standard should first decide which components measured by the instrument are to be used in the evaluation of the performance. These are termed *specified components*. For each specified component, the range of amount fractions over which the response function is to be evaluated shall then be decided.

6.1.2   Specified components

For measurement systems set up to determine the major components in natural gas, the components typically specified are nitrogen, carbon dioxide, methane, ethane, propane, 2-methylpropane (*iso*-butane), *n*-butane, 2-methylbutane (*iso*-pentane) and *n*-pentane. In addition, some analytical requirements include 2,2-dimethylpropane (*neo*-pentane). This component is typically present in very low amounts in natural gas and might not be specified in many systems for measurement. In a typical chromatography method, higher hydrocarbons are often specified as a summed component such as hexanes+ (C_{6+}) where

all hydrocarbons containing six carbon atoms or greater are included in one specified component. The instrumental method may measure such a component as an individual chromatographic peak which is typically backflushed through the system, and all components elute at the same time through the detector. Alternatively, in systems where valve switching is not possible, the heavier hydrocarbons elute in a forward fashion through the columns and the component is simply measured as the sum of individual peaks. However, the system may be set up to measure all hexanes (C_6s) individually and the summed peak C_{7+} may be specified. This is often the case should the C_{6+} amount be significant and a more detailed breakdown of this component be required to minimize errors on the measurement. This principle can be extended such that the system is set up to measure in a C_{6+}, C_{7+}, C_{8+}, C_{9+} or even C_{10+} mode. Users of this International Standard shall decide which of these components are to be included in the evaluation of the instrument's performance based upon the significance of the amounts of each of the components specified in the instrument set-up.

6.1.3   Component content ranges

Once it is clear which measured components are going to be included in the evaluation, the user shall determine, for each of these, over what range of amount fractions the instrument is expected to be used. Such ranges shall generally be greater than that which is expected to be measured by the instrument in regular duty. If the data from the performance evaluation is used subsequently to update the response functions assumed by the instrument, then it is vital that the component content ranges used in the evaluation extend beyond the specified operating range. Should this not be the case, considerable measurement errors might result from extrapolation outside the determined response function.

6.2   Response function types

6.2.1   Assumed functional descriptions

The instrument data system will assume a relationship between response and content of a component in the gas. This is the assumed analysis function of the instrument, $x = G_{asm}(y)$. Many instruments assume a simple first-order polynomial function in the form $x = b_1 y$, where b_1 is often referred to as the response factor (RF) for that component. In this case a single calibration gas mixture is used and a first-order response function is assumed, passing through the origin. Alternatively, the instrument may assume a higher-order polynomial functional description or even an exponential or power function.

In some cases the response, particularly for a minor component, may be calculated as relative to that of another (reference) component. Such a relative response factor shall have a response function similar to that of the reference component.

The assumed analysis function for each component, $x = G_{asm}(y)$, shall be noted and used for subsequent calculation of the instrument's performance characteristics described in 6.6.

The function types considered for the treatment of the performance evaluation data shall be matched to those used by the instrument's data system.

NOTE   Occasionally, functional types other than polynomials, such as exponential relationships, are implemented by an instrument's data system. If the instrument uses functional types other than polynomials, it is appropriate to use these in the determination of the analysis functions. However, for the purposes of this International Standard, only polynomial functions up to third order are considered.

6.2.2   Selection of function types

The type of function to be used in practice is chosen according to the response characteristics of the measuring system and that assumed by the instrument's data system.

Polynomial functions describing the true response/amount fraction relationship can be derived in either domain. A mathematical description of instrument response as a function of amount fraction is termed the *calibration function*, whereas that describing amount fraction as a function of response is termed the *analysis function*.

Hence, the true calibration functions, $F_{i,\text{true}}(x_i)$, determined for each component are in the form

$$y_i = F_{i,\text{true}}(x_i) = a_0 + a_1 x_i + a_2 x_i^2 + a_3 x_i^3 \tag{1}$$

where a_z are the parameters of the calibration function.

Similarly, the true analysis functions, $G_{i,\text{true}}(y_i)$, are in the form

$$x_i = G_{i,\text{true}}(y_i) = b_0 + b_1 y_i + b_2 y_i^2 + b_3 y_i^3 \tag{2}$$

where b_z are the parameters of the analysis function.

In both cases

y_i is the mean response of the instrument to component i;

x_i is the amount fraction of component i.

The response functions above are shown in a form up to third order. However, simpler forms up to second order or simply first order may be considered. Choose the form of the response functions with the following considerations:

a) the simplest form that gives an adequate fit to the data should be used to avoid over-parameterizing the response function;

b) the number of calibration points, and hence the number of reference gases required to satisfactorily describe a polynomial, increases with the order of the function (see 6.4.2);

c) if there is an *a priori* reason to assume that a lower-order polynomial will always be suitable, then this should be chosen and a lower number of reference gases may be used (see 6.4.2).

6.3 Calibration gas reference data

6.3.1 General considerations

The performance benchmarks from this evaluation procedure are calculated for the instrument used in combination with the proposed/current calibration gas mixture. This is the working calibration gas used for routine, often daily, calibration.

NOTE   The design of the calibration gas mixture can have significant influence on the distribution of bias errors for the instrument. Similarly, the uncertainties on the amount fraction of each component in the calibration gas can make a significant contribution to the uncertainty on the measurement results. Hence, the design and uncertainty of composition of the calibration mixture shall be chosen carefully.

6.3.2 Composition and uncertainty

The amount fraction, $x_{i,\text{cal}}$, and standard uncertainty, $u(x_{i,\text{cal}})$, for each component in the calibration gas mixture shall be obtained or derived from the certificate of calibration.

If the uncertainty quoted on the certificate is not a standard uncertainty (k = 1), then the standard uncertainties shall be derived using the manufacturer's stated coverage factor.

$$u(x_{i,\text{cal}}) = U_{\text{cert}}(x_{i,\text{cal}}) / k \tag{3}$$