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Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration

Analyse des gaz — Méthodes de comparaison pour la détermination de la composition des mélanges de gaz basées sur un ou deux points **iTeh ST**d'étalonnagerd PREVIEW

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Contents

Page

Forew	ord		iv	
Introd	uction		v	
1	Scope		1	
2	Norma	itive references	1	
3	Terms	and definitions	1	
4	Symbo	ls	2	
5	Abbre	viated terms	2	
6	Princi	nle	3	
0	6.1 6.2	General requirements Calibration methods	3 4	
7	Main procedure			
	7.1	Pre-requisites	4	
	7.2 7.3	Calibration and measurement designs	4 5	
	/10	7.3.1 General	5	
		7.3.2 Single-point exact-match calibration (SPEM)	6	
		7.3.3 Single-point through origin calibration (SPO)	6	
		7.3.4 Two-point calibration with a blank (TPB)	7 7	
		7.3.6 Multipoint calibration (MPG) to be at	7	
8	Perfor	mance evaluation of the measuring system	8	
U	8.1	General	8	
	8.2	Sources of performance evaluation data and alternative approach	11	
		8.2.1 Performance evaluation other than in-house	11	
		8.2.2 Alternative for performance evaluation	11	
9	Quality assurance measures			
	9.1	Validation of the assumptions made	11	
4.0	5.2 Dring stability control of the measuring system			
10	10.1 Calibration gas cortificatos			
	10.1	Report of analysis	12	
Annex	A (nor	mative) System-stability check required when using exact-match and		
	brack	eting designs	13	
Annex	B (nor	mative) Statistics and sensitivity coefficients used in <u>Clause 7</u>	15	
Annex	C (nor	native) Alternative approach to assessing the nonlinearity contribution	17	
Annex	D (info	rmative) Worked-out example	19	
Annex	E (info	rmative) Using the designs without preceding system performance evaluation	22	
Biblio	graphy		24	

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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 on 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 the following URL: www.iso.org/iso/foreword.html. (standards.iteh.ai)

This document was prepared by Technical Committee ISO/TC 158, Analysis of gases.

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Introduction

Whereas the comparison methods described in ISO 6143 based on multipoint calibration are in principle suited for all applications in gas analysis for determining the composition of calibration gas mixtures, in many cases, simpler calibration methods can be used. These methods typically require a smaller number of calibration gas mixtures with a traceable composition.

One- and two-point calibration of instruments is widely used in the gas industry and in national metrology institutes. They often constitute fair compromise between costs and efforts on one hand, and accuracy on the other. These simpler methods require validation to confirm that the conditions of use are appropriate.

It is the intention of this document to set up and describe comparison methods and data evaluation techniques based on one- and two-point calibration. The applicable conditions and limitations of the methods are derived from the analytical requirements and are clearly specified.

This document describes the assessment, calculation and expression of measurement uncertainty arising from significant contributors in the different comparison methods.

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Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and twopoint calibration

1 Scope

2

This document provides methods for

- calibrating an instrument with one or two calibration gas mixtures,
- determining the composition of a gas sample, and
- evaluating the uncertainty of the composition of the gas sample in relation to the uncertainty of the composition of the calibration gases used and the contribution of the measurement process.

This document sets requirements to, and acceptance criteria for, the utilization of different measurement calibration designs with a limited (i.e. minimum) number of calibration gas mixtures used in calibration.

The methods in this document are described for amount-of-substance fractions, but are also applicable for other composition quantities (such as mass fractions, volume fractions or concentrations).

Normative references (standards.iteh.ai)

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 6141, Gas analysis — Contents of certificates for calibration gas mixtures

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

ISO 7504, Gas analysis — Vocabulary

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

ISO/IEC Guide 99, International vocabulary of metrology — Basic and general concepts and associated terms (VIM)

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 7504, ISO/IEC Guide 98-3 and ISO/IEC Guide 99 apply.

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

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

4 Symbols

- α_j coefficients of the best available calibration function f(j = 0, 1, ..., N) with $N \le 3$ as determined in the performance evaluation procedure, with N being the order of the polynomial
- b_j parameters of the simplified analysis function g (j = 0, 1)
- β_j parameters of the best-available analysis function g (j = 0, 1, ..., N) with $N \le 3$ as determined in the performance evaluation procedure, with N being the order of the polynomial
- f calibration function, y = f(x)
- *g* analysis function, x = g(y)
- *k* coverage factor
- *m* number of replicate measurements taken
- *N* order of the polynomial
- *R* range of amount-of-substance fractions within which the selected method of calibration is applied to samples of unknown composition (hereinafter: unknown samples)
- U(q) expanded uncertainty associated with the quantity, q, $U(q) = k \times u(q)$
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- u(q) standard uncertainty associated with the quantity, q
- $u(\Delta)$ uncertainty contribution due to zero-deviations and analyser nonlinearity https://standards.iteh.ai/catalog/standards/sist/e275f856-d9c1-4b52-8ea9-
- $u^2(q)$ variance associated with the quantity, $q^{648/iso-12963-2017}$
- *x* amount fraction
- (x_i, y_i) calibration point(s) (i = 1, 2, ..., n), with *n* being its number
- $y_{(l)}$ instrumental response, with *l* indicating the replicate number
- \overline{y} mean replicated instrumental responses
- *Γ* goodness of fit; a measure of local compatibility of a calibration point with the calculated calibration or analysis function
- Δ bias due to zero-deviation and analyser nonlinearity
- δ bias
- $\overline{\delta}$ average bias

5 Abbreviated terms

- b blank
- GLS generalized least squares
- MPC multipoint calibration

Re	measurement of the matching reference
r	subscript denoting a calibration gas mixture
r1, r2	calibration gas mixtures bracketing the composition of the unknown sample
S	unknown gas sample
S	subscript denoting an unknown gas sample
SSD	sum of weighted squared deviations
SPEM	single-point exact-match calibration
SPO	single-point through origin calibration
ТРВ	two-point calibration using a single point and a blank
ТРС	two-point calibration

6 Principle

6.1 General requirements

The composition of a gasemixture is determined by separate measurement of the amount fraction of every specified component. "Separate" implies that the response obtained for the component of interest is treated independently of any other response obtained for any other component. It does not impede obtaining several responses for several components in the same instrument run. Therefore, the procedure for determining the amount fraction of only one specified component is described. Possible interferences of other components on the measurement of the component of interest shall be avoided or corrected for separately. This subject is not further addressed in this document.

The procedure for determining the amount fraction *x* of a specified component *X* in a sample of a gas mixture, or in a series of such samples, is performed in a sequence of steps as summarized below.

- a) Specify the analytical range of interest, *R*, i.e. the range of the amount fraction *x* to be determined, and the acceptable or required (if applicable) uncertainty level.
- b) Specify the analytical method and the measuring system to be used:
 - 1) calibration range (to encompass the analytical range);
 - 2) composition, including uncertainty, of the calibration gas mixtures;
 - 3) parameters of the analytical method;
 - 4) measuring conditions;
 - 5) number and sequence of calibration measurements (see <u>8.1</u>).
- c) Select, from the list given in <u>6.2</u>, an approach for calibration and determining the amount fractions of components in unknown samples in the regular, i.e. daily mode when one- and two-point based analysis functions are used.
- d) For the relevant ranges of responses and component amount fractions, determine the uncertainty level of the prospective results based on the analysis function. If the result is acceptable, performance evaluation was successful.

For the calculation of the measurement uncertainty of results obtained in the regular calibration mode, an estimate $u(\Delta)$ for the contribution of possible nonlinearity of the system is needed. This estimate is calculated in a performance evaluation of the system according to <u>Clause 8</u> and <u>Annex C</u>.

The evaluation is best done after the specifications according to a) to c) are set. The estimate is used in all subsequent regular calibrations until there is reason to assume significant changes in the instrument performance. The main reasons for such changes are given in 9.1.

e) Perform calibration and measurement according to the steps given in <u>Clause 7</u>.

6.2 Calibration methods

The following calibration methods for determining the amount fraction of a specified component in an unknown gas sample may apply:

- a) single-point exact-match calibration (SPEM) and direct transfer of value and uncertainty of the matching calibration gas mixture;
- b) single-point through origin calibration (SPO) and transfer of the value assuming a straight-line calibration function through the origin;
- c) two-point calibration using a single-point and a blank (TPB) calculation of the value from a straightline analysis function;
- d) two-point calibration: bracketing using two calibration gas mixtures (TPC).
- NOTE Multipoint calibration (MPC) uses at least three calibration points.

7 Main procedure iTeh STANDARD PREVIEW

7.1 Pre-requisites

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Stability of the system within the period of time equal to a normal calibration interval shall be demonstrated during method validation. The use of unstable systems is strongly discouraged in general, in particular for designs SPO and TPB in 6.2. For use of designs SPEM and TPC with not sufficiently stable systems, see Annex A.

7.2 Sequence of operations (overview)

<u>Figure 1</u> illustrates the basic steps of carrying out measurements according to the calibration methods described in this document. Aims, steps and frequency of the performance evaluation are described in <u>Clause 8</u>.



7.3 Calibration and measurement designs

7.3.1 General

All designs as specified in 6.2 consist of four basic steps, namely

- step A: calibration of the instrument;
- step B: measurement of the sample;
- step C: calculation of the unknown amount fraction of the component in the sample;
- step D: calculation of the uncertainty of the amount fraction of the component.

In practice, steps A and B apply in order to adjust the calibration gas mixture to the unknown sample, in particular for SPEM and SPO. For SPEM, the calibration gas mixture shall resemble the unknown (see 7.3.2); for SPO, the measured response of the sample shall be in the predefined range in the vicinity of the response of the calibration gas mixture.

For all designs, at least three replicates should be taken for any unknown or calibration gas mixture, whenever practicable. Such a number should be sufficient to confirm adequate repeatability of the responses. If three replicates are not feasible, the user shall have a reliable estimate of the standard uncertainty of the sample measurement.

Expressions for the mean and the standard deviations of replicate signal measurements used throughout this document are given in <u>Annex B</u>.

7.3.2 Single-point exact-match calibration (SPEM)

Step A: Select a calibration gas mixture such that the measuring system produces, on this mixture, responses which are statistically indistinguishable from those obtained on the unknown sample.

Take at least three replicate measurements of the calibration gas mixture and calculate the mean response value of these replicates, y_r , and the standard uncertainty, $u(y_r)$, of the mean response value (see <u>Annex B</u>).

Step B: Take at least three replicate measurements of the sample and calculate the mean response value of these replicates, y_s , and the standard uncertainty, $u(y_s)$, of the mean response value (see <u>Annex B</u>).

Calibration gas and sample are indistinguishable if it holds

$$\frac{|y_{\rm r} - y_{\rm s}|}{2 \times \sqrt{u^2(y_{\rm r}) + u^2(y_{\rm s})}} \le 1$$
(1)

Step C: If the condition according to Formula (1) is fulfilled, the value of the unknown is estimated by direct transfer of the value of the calibration gas mixture, i.e. it holds

$$x_{\rm s} = x_{\rm r} \cdot \frac{y_{\rm s}}{y_{\rm r}} \tag{2}$$

In an exact-match situation, the signal ratio for the measurements of the unknown and the reference should ideally be unity, yielding the "exact" match, $x_s = x_r$. Formula (2) thus accounts for situations rather at the edges of the condition according to Formula (1).

Step D: Repeat the measurements with the calibration gas mixture in order to check system stability in accordance with <u>Annex A</u>.

Step E: The uncertainty of the value of the unknown is derived from the uncertainty of the calibration gas mixture by direct transfer, taking into account that measurements are carried out on both the calibration and the unknown gas sample; see Formula [3]:

$$u^{2}(x_{s}) = u^{2}(x_{r}) + \frac{x_{r}^{2}}{y_{r}^{2}} \cdot \left[u^{2}(y_{s}) + u^{2}(y_{r})\right]$$
(3)

7.3.3 Single-point through origin calibration (SPO)

Step A: Select a calibration gas mixture such that the measuring system produces, on this mixture, responses which are sufficiently close to those obtained on the unknown sample. Closeness is characterized by the pre-selected range, *R*. A calibration gas may be considered sufficiently close to the unknown sample if the amount fraction of the component of interest does not differ by more than +50 % or -10 % from the unknown sample.

Take at least three replicate measurements of the calibration gas mixture and calculate the mean response value of these replicates, y_r , and the standard uncertainty, $u(y_r)$, of the mean response value (see <u>Annex B</u>).

Step B: Take at least three replicate measurements of the sample and calculate the mean response value of these replicates, y_s , and the standard uncertainty, $u(y_s)$, of the mean response value (see <u>Annex B</u>).

Step C: The value of the unknown is calculated by assuming a straight-line analysis function through the origin and calculated from the value of the calibration gas mixture according to <u>Formula (4)</u>:

$$x_{\rm s} = b_1 \times y_{\rm s} \tag{4}$$

where b_1 denotes the slope of the analysis function, i.e. the ratio x_r/y_r .