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Stationary source emissions — Demonstration of equivalence of an alternative method with a reference method

National foreword

This British Standard is the UK implementation of EN 14793:2017. It supersedes DD CEN/TS 14793:2005 which is withdrawn.

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Émissions de sources fixes - Démonstration de l'équivalence d'une méthode alternative avec une méthode de référence

Emissionen aus stationären Quellen - Nachweis der Gleichwertigkeit eines Alternativverfahrens mit einem Referenzverfahren

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European foreword

This document (EN 14793:2017) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document supersedes CEN/TS 14793:2005.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2017, and conflicting national standards shall be withdrawn at the latest by July 2017.

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Introduction

Much has been published in the literature concerning method validation by collaborative study. CEN/TC 264 working groups try to follow these method validations when a new standard is prepared and the collaborative study is probably the preferred way of carrying out the validation. However, it is not always a suitable option for accredited laboratories. The application for which the method is required can be esoteric to the extent that no other laboratories would be interested in collaboration. Those that might be interested can be competitors.

This European Standard provides one of possible methods of testing the equivalence of an alternative method (AM) with the standard reference method (SRM) or with a reference method (RM) if the legislator has not defined a standard reference method.

NOTE The term “reference method” is used in this standard to cover reference methods as well as standard reference methods.

In the framework of certification of automated measuring systems used for the measurement of stationary source emissions this European Standard can be used in conjunction with EN 15267-4:2017 to demonstrate the equivalence of portable automated measuring systems (P-AMS) based on an AM with the standard reference method (SRM).

1 Scope

This European Standard specifies a procedure to demonstrate the equivalence of an alternative method (AM) with the reference method (RM) or the standard reference method (SRM), both implemented to determine the same measurand.

In particular, this European Standard provides the statistical tools and different criteria to evaluate the alternative method. This does not release the body performing the equivalence testing from bearing technical and analytical judgement on the evaluation of the different criteria.

Three steps are required for demonstration of equivalence:

- description of the alternative method and setting of the field of application (measurement range and type of gas matrix);
- determination of the performance characteristics of the alternative method and calculation of the expanded uncertainty where appropriate and check of compliance with the maximum expanded uncertainty allowed for the reference method;
- check of repeatability and lack of systematic deviation of the alternative method in the field or on a recognized test bench in comparison with the reference method for the type of matrix defined in the field of equivalence.

This European Standard requires that a reference method has been defined and validated.

This European Standard only considers the case of linear quantitative methods.

This European Standard is applicable to manual and automated methods.

This European Standard has been drawn up for laboratories working in air quality measurements and consequently an example taken from this sector are presented in Annex A.

2 Normative references

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

EN ISO 14956, *Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956)*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

3 Terms and definitions

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

3.1
standard reference method
SRM
reference method prescribed by European or national legislation

[SOURCE: EN 15259:2007]

Note 1 to entry: Standard reference methods are used e.g. to calibrate and validate automated measuring systems permanently installed at stacks and for periodic measurements to check compliance with limit values.

3.2
reference method
RM
measurement method taken as a reference by convention, which gives the accepted reference value of the measurand

Note 1 to entry: A reference method is fully described.

Note 2 to entry: A reference method can be a manual or an automated method.

Note 3 to entry: Alternative methods can be used if equivalence to the reference method has been demonstrated.

[SOURCE: EN 15259:2007]

3.3
alternative method
AM
measurement method which complies with the criteria given by this European Standard with respect to the reference method

Note 1 to entry: An alternative method can consist of a simplification of the reference method.

3.4
measurement method
method described in a written procedure containing all the means and procedures required to sample and analyse, namely field of application, principle and/or reactions, definitions, equipment, procedures, presentation of results, other requirements and measurement report

3.5
calibration
set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring method or measuring system, and the corresponding values given by the applicable reference

3.6
accepted reference value
value which serves as a reference value (or conventionally true value) of the sample, provided by the reference method or standard reference method

3.7
demonstration of equivalence

act of subjecting a measurement method to a study, which is based on a standardised and/or recognised protocol and which provides proof that, for its field of application, the measurement method satisfies pre-established performance criteria

Note 1 to entry: In the framework of this European Standard, the demonstration of equivalence of a method is mainly based on an “in field” study that includes comparison to a reference method.

3.8
field of application

combination of the different types of matrix and the range of concentrations of the measured component covered, to which the measurement method is applied

Note 1 to entry: As well as being an indication of all the satisfactory performance conditions for each factor, the field of application of the measurement method can also include warnings concerning known interferences caused by other components, or the inapplicability of certain matrices or conditions.

3.9
matrix

all the components of the sample other than the measured component

Note 1 to entry: Some components of the matrix can influence the result of measurement. These components are called interferents.

3.10
measurand

particular quantity subject to measurement

[SOURCE: EN 15259:2007]

Note 1 to entry: The measurand is a quantifiable property of the stack gas under test, for example mass concentration of a measured component, temperature, velocity, mass flow, oxygen content and water vapour content.

3.11
measured component

constituent of the waste gas for which a defined measurand is to be determined by measurement

[SOURCE: EN 15259:2007]

Note 1 to entry: Measured component is also called determinand.

3.12
reference material

substance or mixture of substances, with a known concentration within specified limits, or a device of known characteristics

3.13
linearity

capacity of a measurement method, within certain limits, to provide an instrument response or results proportional to the quantity of the measurand to be determined in the sample

Note 1 to entry: This proportionality is expressed through a defined a priori mathematical expression.

Note 2 to entry: The linearity limits are the concentration limits in the experiment between which a linear calibration model can be applied with a known level of confidence.

3.14
lack of fit

systematic deviation, within the measurement range, between the accepted value of a reference material applied to the measuring system and the corresponding result of measurement produced by the calibrated measuring system

Note 1 to entry: In common language lack of fit is often called “linearity” or “deviation from linearity”. Lack of fit test is often called “linearity test”.

3.15
detection limit

L_D

smallest quantity of the measurand which can be detected, but not quantified, in the experiment conditions described for the measurement method

3.16
quantification limit

L_Q

smallest quantity of the measurand which can be quantified, in the experiment conditions described for the measurement method

3.17
repeatability

closeness of agreement between independent test results obtained under stipulated conditions

Note 1 to entry: Repeatability depends exclusively upon the distribution of random errors and has no relation with the true or specified value.

Note 2 to entry: The measure of repeatability is calculated from the standard deviation of test results. A lower level of repeatability is reflected by a greater standard deviation.

Note 3 to entry: The term “independent test results” signifies results obtained in such a way as not to be influenced by a previous result on the same or similar testing equipment. Quantitative measurements of repeatability depend critically upon the stipulated conditions. Repeatability and reproducibility conditions are specific groups of extreme conditions.

3.18
trueness

closeness of agreement between the average value obtained from a large series of test results and an accepted reference value

[SOURCE: ISO 5725-1:1994]

Note 1 to entry: The measure of trueness is generally expressed in terms of a bias or a systematic deviation.

4 Symbols

For the purpose of this document, the symbols listed in Table 1 apply.

Table 1 — Symbols and formulae

Symbol	Description	Formula
C_0	intercept of the orthogonal regression line between AM and RM values	$C_0 = \overline{\overline{x}} - \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}\overline{\overline{z}}$
C_1	slope of the orthogonal regression line between AM and RM values	$C_1 = \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}$
$\mathrm{d}x_i$	difference between x_{i1} and x_{i2} for each value of *i*	$\mathrm{d}x_i = \left(x_{i1} - x_{i2}\right)$
e_i	ratio between $\mathrm{d}x_i$ and $\overline{x}_i$ for each value of *i*	$e_i = \frac{\mathrm{d}x_i}{\overline{x}_i}$
$\overline{e}$	average value of the values e_i	$\overline{e} = \frac{\sum_{i=1}^{n} e_i}{n}$
G_i	ratio between $\left(e_i - \overline{e}\right)$ and $s\left(e_i\right)$	$G_i = \frac{\left\|e_i - \overline{e}\right\|}{s\left(e_i\right)}$
L_D	detection limit	
L_Q	quantification limit	
p	number of trials	
n_i	number of parallel measurement for the AM and for the RM for a trial *i*	
N	total number of measurements for the AM and for the RM	$N = \sum_{i=1}^{p} n_i$
r	correlation coefficient	$r = \frac{\mathrm{SPD}(\overline{\overline{x}}, \overline{\overline{z}})}{\sqrt{\mathrm{SSD}(\overline{\overline{x}}) \times \mathrm{SSD}(\overline{\overline{z}})}}$
$s\left(e_i\right)$	standard deviation of the population of the e_i	$s\left(e_i\right) = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(e_i - \overline{e}\right)^2}$
$s^2\left(\overline{\overline{x}}\right)$	variance of the AM	$s^2\left(\overline{\overline{x}}\right) = \frac{\mathrm{SSD}\left(\overline{\overline{x}}\right)}{p-1}$
$s_r\left(\overline{\overline{x}}\right)$	repeatability standard deviation of the AM	

$s_r^2\left(\overline{\overline{x}}\right)$	repeatability variance of the AM	$s_r^2\left(\overline{\overline{x}}\right)=\dfrac{\sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(x_{ij}-\overline{x}_i\right)^2}{N-p}$.
$s^2\left(\overline{\overline{z}}\right)$	variance of the RM	$s^2\left(\overline{\overline{z}}\right)=\dfrac{\mathrm{SSD}\left(\overline{\overline{z}}\right)}{p-1}$
$s_r\left(\overline{\overline{z}}\right)$	repeatability standard deviation of the RM	
$s_r^2\left(\overline{\overline{z}}\right)$	repeatability variance of the RM	$s_r^2\left(\overline{\overline{z}}\right)=\dfrac{\sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(z_{ij}-\overline{z}_i\right)^2}{N-p}$
$s_{r,\mathrm{limit}}\left(\overline{\overline{z}}\right)$	maximum allowable repeatability standard deviation for the RM	
$s_R\left(\overline{\overline{z}}\right)$	reproducibility standard deviation given in the RM standard	
$\mathrm{SPD}\left(\overline{\overline{x}},\overline{\overline{z}}\right)$	sum of the products of the deviations for two variables $\overline{x}$ and $\overline{z}$	$\mathrm{SPD}\left(\overline{\overline{x}},\overline{\overline{z}}\right)=\sum_{i=1}^{p}\left(\overline{x}_i-\overline{\overline{x}}\right)\times\left(\overline{z}_i-\overline{\overline{z}}\right)$
$\mathrm{SSD}\left(\overline{\overline{x}}\right)$	sum of the squares of the mean deviations for the AM	$\mathrm{SSD}\left(\overline{\overline{x}}\right)=\sum_{i=1}^{p}\left(\overline{x}_i-\overline{\overline{x}}\right)^2$
$\mathrm{SSD}\left(\overline{\overline{z}}\right)$	sum of the squares of the mean deviations for the RM	$\mathrm{SSD}\left(\overline{\overline{z}}\right)=\sum_{i=1}^{p}\left(\overline{z}_i-\overline{\overline{z}}\right)^2$.
U_{RM}	maximum permissible expanded uncertainty given in the RM standard	
x_{ij}	concentration obtained by the AM for a trial *i* and repetition *j*	
$\overline{x}_i$	arithmetic mean of x_{ij} for which n_i measurements have been taken	$\overline{x}_i=\dfrac{\sum_{j=1}^{n_i}x_{ij}}{n_i}$
$\overline{\overline{x}}$	grand average of x_{ij} for which N measurements have been taken	$\overline{\overline{x}}=\dfrac{\sum_{i=1}^{p}\sum_{j=1}^{n_i}x_{ij}}{N}$
x_p	outlier	
z_{ij}	concentration obtained by the RM for a trial *i* and repetition *j*	
$\overline{z}_i$	arithmetic mean of z_{ij} for which n_i measurements have been taken	$\overline{z}_i=\dfrac{\sum_{j=1}^{n_i}z_{ij}}{n_i}$

$\overline{\overline{z}}$	grand average of z_{ij} for which N measurements have been taken	$\overline{\overline{z}} = \frac{\sum_{i=1}^{p}\sum_{j=1}^{n_i} z_{ij}}{N}$
z_q	outlier	

5 Contents of the demonstration of equivalence

5.1 General

The demonstration of equivalence shall include the following items:

- description of the alternative method (see 5.2);
- determination of performance characteristics (see 5.3);
- calculation of the expanded uncertainty of the alternative method (see 5.4);
- demonstration of equivalence in the field (see 5.5).

WARNING 1 The field of application of an alternative method can partially or completely cover the field of application of the reference method. However, if it covers the fields of application of several reference methods (horizontal method), several evaluations of each reference method shall be performed, e.g. in the case of multi-component measurement methods like FTIR.

WARNING 2 The definition of the field of application depends entirely upon the laboratory applying the alternative method and the knowledge acquired during the development of the method. It is sometimes preferable to segment a field of application rather than to attempt to validate an overly general method. In this case, a validation file for each field of application shall be compiled.

5.2 Description of the alternative method

The description shall permit all competent persons to use it (including the procedure and the calculations). The following items should be addressed:

- title;
- warnings and safety precautions (where relevant);
- introduction;
- purpose and field of application;
- standard references;
- definitions;
- principle (sampling and analysis);
- reagents and products (where relevant);
- equipment (e.g.: description of the sampling line and measuring device);
- procedures for quality checks;
- definition of performance characteristics and determination procedures;

- presentation of results;
- specific cases;
- remarks;
- test report;
- annexes;
- bibliography.

The field of application of the alternative method shall be clearly defined in terms of:

- measured component;
- gas matrixes;
- concentration range (the limit of quantification and the upper limit of the claimed concentration range shall be given);
- external conditions (e.g. ambient temperature).

NOTE Some of the above items might not be applicable to a specific method.

5.3 Determination of performance characteristics

5.3.1 General

The performance characteristics shall be determined in accordance with the description of the alternative method. Identify all potentially important sources of uncertainty in accordance with relevant standards. Any performance characteristic that is not able to create a standard uncertainty of more than 5 % of the highest standard uncertainty of the others may be excluded from the selection.

5.3.2 Manual method

Main sources of uncertainty for manual methods are attached to:

- absorption efficiency of the absorption bottles;
- calibration of the gas volume meter;
- effect of temperature variation in the gas meter;
- effect of ambient pressure variation in the gas meter;
- humidity after the drying cartridge;
- leakage of the sampling line;
- absorption in the sampling system;
- preparation of sample for analysis;
- analysis;

- limit of detection and quantification;
- lack of fit;
- repeatability;
- interferences;
- calibration procedure;
- reference materials.

5.3.3 Automatic method

Main sources of uncertainty for automated methods are attached to:

- response time;
- limit of detection and quantification;
- lack of fit;
- drift on a duration adapted to the measurement purpose;
- repeatability;
- dependence on sampling gas pressure;
- dependence on ambient temperature;
- dependence on voltage;
- interferences;
- leakage of the sampling line;
- absorption in the sampling system;
- adjustment of the analyser;
- reference material (e.g. calibration gas).

5.4 Calculation of the expanded uncertainty of the AM

The expanded uncertainty of the AM shall be calculated by building an uncertainty budget according to EN ISO 14956 or ISO/IEC Guide 98-3 (GUM). The maximum expanded uncertainty of the alternative method shall be compared with the reference's and shall be lower or equal to the maximum expanded uncertainty specified by the reference method at the emission limit value.

5.5 Demonstration of equivalence in the field

5.5.1 Coverage of in field demonstration

5.5.1.1 General

The demonstration of equivalence in the field shall be performed at suitable plant(s). If necessary, a combination of two sets of data drawn from trials performed on plant(s) and on a test bench recognized by the competent authorities and meeting the requirements in Annex C may be used.

5.5.1.2 Gas matrixes

The "in field demonstration" covers the field of application of the method defined under the sole responsibility of the test laboratory. In practice, it is the responsibility of the laboratory to demonstrate that the field of application of the method is correctly covered, in terms of types of matrixes. The laboratory may determine the effect of each of the individual compounds present in the flue gases suspected to have an influence on the measurement result. Nevertheless, this experimental work in the laboratory cannot cover all the compounds that could interfere with the measurement results. Therefore, the possible effect of interferences shall be checked against the reference during experiment in the field by implementing both methods in parallel. The laboratory shall find suitable plant(s), where the gas matrix containing high level of interfering gases of the stack gas exists. If the comparison with the reference method shows that the alternative method is valid and if there are no technical reasons against it, the transfer of the validity from this type of plant to other kinds of plants shall be made regular.

NOTE In the type approval or certification scheme for emission measurements, it is agreed that if the suitability of a method is demonstrated on a waste incineration, then this suitability can be extended to other types of plants with different gas matrixes like combustion or co-combustion plants.

5.5.1.3 Concentration range

If the alternative method has shown in the laboratory an acceptable linearity (see 5.3) and expanded uncertainty (see 5.4) then the comparison in the field does not need to be carried out on the whole claimed concentration range where linearity has been checked. However, to be relevant, the statistical test for checking if there is no systematic deviation between AM and RM measurements, perform measurements in the field over all the claimed concentration range. At least 30 % of the total number of parallel measurements shall be performed in the lower 20 % of the range and at least 30 % in the upper third of the range. Criteria of acceptance of the demonstration are given in 5.5.2.3.3.

To perform the demonstration and succeed to study a large concentration range, a combination of two sets of data drawn from trials performed on one or several plants of the same type can be accepted. An alternative might be to perform the comparison on a test bench recognized by the competent authorities to be able to generate the appropriate gas matrix. In this case, the test bench shall meet the requirements in Annex C.

If the claimed concentration range has not been chosen correctly, it can be limited, particularly if the repeatability or systematic deviation studies show that it is not possible to fulfil the criteria for acceptance of repeatability and trueness across the whole range of concentrations. In such cases, the AM shall be validated in one or more limited set of conditions. A validation file fulfilling the criteria for acceptance of the demonstration given in 5.5.2.2 and 5.5.2.3.3 is required for each range of concentration.

5.5.2 Evaluation of repeatability and trueness in relation to the RM

5.5.2.1 Organization

In field demonstration of equivalence enables the comparison of repeatability standard deviations (see Table 2) and the determination of the regression line between AM and RM results to evaluate systematic deviation (trueness) in relation to the RM.

To obtain comparison data of the AM and RM, perform simultaneously at least 30 measurements with the AM and with the RM, so that Table 2 can be drawn up. The number n_i shall be at least two (paired measurements) and should be identical for each trial *i*.

Table 2 — Organization of the in field demonstration

Alternative method								
Trials	**Parallel measurements**				**Number of measurements**	**Means**	**Variances**	
	1	2	...	n_i	n_i	$\bar{x}_i$	$s^2\left(\bar{x}_i\right)$.	
1	x_{11}	x_{12}	...	x_{1n_1}	n_1	$\bar{x}_1$	$s^2\left(\bar{x}_1\right)$	
...	...	...	...	...	...	...	...	
i	x_{i1}	x_{i2}	...	x_{in_i}	n_i	$\bar{x}_i$	$s^2\left(\bar{x}_i\right)$	
...	...	...	...	...	...	...	...	
p	x_{p1}	x_{p2}	...	x_{pn_p}	n_p	$\bar{x}_p$	$s^2\left(\bar{x}_p\right)$	
Reference method								
Trials	**Parallel measurements**				**Number of measurements**	**Means**	**Variances**	**Differences**
	1	2	...	n_i	n_i	$\bar{z}_i$	$s^2\left(\bar{z}_i\right)$	$\bar{x}_i - \bar{z}_i$
1	z_{11}	z_{12}	...	z_{1n_1}	n_1	$\bar{z}_1$	$s^2\left(\bar{z}_1\right)$	$\bar{x}_1 - \bar{z}_1$
...	...	...	...	...	...	...	...	
i	z_{i1}	z_{i2}	...	z_{in_i}	n_i	$\bar{z}_i$	$s^2\left(\bar{z}_i\right)$	$\bar{x}_i - \bar{z}_i$
...	...	...	...	...	...	...	...	
p	z_{p1}	z_{p2}	...	z_{pn_p}	n_p	$\bar{z}_p$	$s^2\left(\bar{z}_p\right)$	$\bar{x}_p - \bar{z}_p$

5.5.2.2 Repeatability

Perform the calculations following the principle described in ISO 5725-2 according to the formulae given in Table 1. Apply them separately to each series of data and calculate the repeatability variances $s_r^2\left(\bar{\bar{x}}\right)$ and $s_r^2\left(\bar{\bar{z}}\right)$ for the AM and the RM. The two standard deviations $s_r\left(\bar{\bar{x}}\right)$ and $s_r\left(\bar{\bar{z}}\right)$ are deduced from these variances.

Acceptance criteria for repeatability of the AM and RM in Formula (1) and Formula (2) shall be met:

$$s_r\left(\overline{\overline{x}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{z}}\right) \quad (1)$$

$$s_r\left(\overline{\overline{z}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{z}}\right) \quad (2)$$

where the value of $s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$ is obtained from an equation of the maximum allowable repeatability standard deviation given in the RM standard. If this value is not specified in the RM standard, the laboratory shall determine this value from the standard deviation of the paired measurements of the RM.

5.5.2.3 Trueness

5.5.2.3.1 General

The trueness of the AM is demonstrated on the basis of a linear relation between the two series of data obtained by the RM and AM with a slope close to one and an intercept close to zero (see criteria of acceptance in 5.5.2.3.3).

In most cases the classical linear regression cannot be used because the uncertainty attached to each result given by the RM is not always negligible compared to the uncertainty of individual results given by the AM. Consequently, the orthogonal linear regression model shall be used.

The regression line is computed so that the sum of the square orthogonal distances between the points and the line is minimal.

The orthogonal regression is symmetrical in *x* and *z* and does not depend on the way the points have been plotted (see Figure 1).

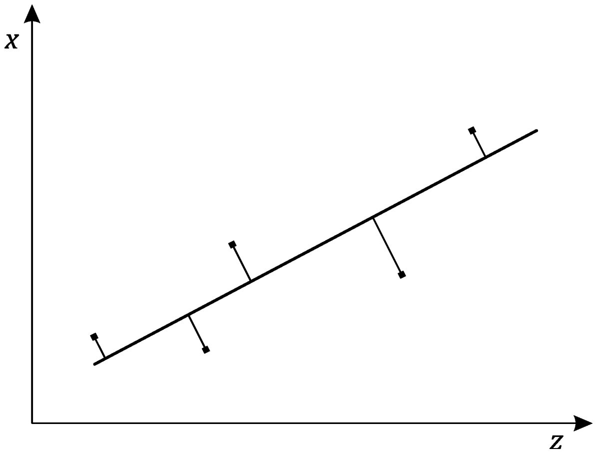

Figure 1 — Illustration of orthogonal linear regression

The orthogonal linear relation between variables *x* and *z* is given by Formula (3):

$$\overline{x}_i = C_0 + C_1\overline{z}_i \quad (3)$$

where

$$C_0 = \overline{\overline{x}} - \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}\overline{\overline{z}} \quad (4)$$

$$C_1 = \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)} \tag{5}$$

5.5.2.3.2 Determination of outliers by Grubbs test

When a pair of results $\left(x_{p1}, x_{p2}\right)$ or $\left(z_{p1}, z_{p2}\right)$ is suspected to be an outlier, take the series of results $\left(x_{p1}, x_{p2}\right)$ or $\left(z_{p1}, z_{p2}\right)$ and calculate:

— the average value $\overline{x}_i$ (or $\overline{z}_i$) for each value of *i*:

$$\overline{x}_i = \frac{\left(x_{i1} + x_{i2}\right)}{2} \tag{6}$$

— the value dx_i of difference between x_{i1} and x_{i2} for each value of *i*:

$$dx_i = \left(x_{i1} - x_{i2}\right) \tag{7}$$

— the relative value e_i of ratio between dx_i and $\overline{x}_i$ for each value of *i*:

$$e_i = \frac{dx_i}{\overline{x}_i} \tag{8}$$

— the average value $\overline{e}$ of the population e_i and the standard deviation s_{ei}:

$$\overline{e} = \frac{\sum_{i=1}^{n} e_i}{n} \tag{9}$$

$$s_{ei} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(e_i - \overline{e}\right)^2} \tag{10}$$

— the value G_i for each value of *i*:

$$G_i = \frac{\left|e_i - \overline{e}\right|}{s_{ei}} \tag{11}$$

Then compare the value of extremum G_p with the critical value given by the table of Grubbs test with a level of confidence of 95 %. The critical values are given in Table B.1.

If the value G_p is greater than the Grubbs critical value, then the values x_{p1} and x_{p2} are potential outliers.

If the Grubbs test detects potential outliers, they may be skipped only if an investigation leads to conclude on laboratory failures.

A maximum of two data pairs for 30 parallel measurements may be skipped.

5.5.2.3.3 Acceptance of trueness

The test on trueness shall be performed only if the acceptance criterion for the test is fulfilled:

$$r \geq 0{,}97 \tag{12}$$

NOTE To fulfil the criterion on *r*, it can be necessary to perform more than 30 parallel measurements on a large concentration range.

To accept the hypothesis that no systematic deviation exists between AM and RM the following acceptance criteria shall be fulfilled where the expressions are calculated at the average value $\overline{\overline{z}}$ of the claimed concentration range and $s_R\left(\overline{\overline{z}}\right)$ is the reproducibility standard deviation whose expression is given in the RM standard:

$$1-\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}} \leq C_1 \leq 1+\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}} \tag{13}$$

and

$$\left|C_0\right| \leq s_R\left(\overline{\overline{z}}\right) \tag{14}$$

If $s_R\left(\overline{\overline{z}}\right)$ is not specified in the RM standard, the laboratory shall determine this value from the expanded uncertainty U_{RM} according to Formula (15):

$$s_R\left(\overline{\overline{z}}\right)=\frac{U_{\mathrm{RM}}}{2} \tag{15}$$

where U_{RM} is the maximum allowable expanded uncertainty specified by the RM. If the value is not given by the RM, the value specified by the measurement objective shall be used.

6 Report of the demonstration of equivalence

The report shall include the results of the following items:

- description of the alternative method (see items in 5.2);
- determination of performance characteristics (see items in 5.3);
- calculation of the expanded uncertainty of the alternative method (see items in 5.4);
- demonstration of equivalence in the field (see items in 5.5).

The section of the report on demonstration of equivalence in the field shall present the raw data and shall summarize the results in tables similar to Table 3 and Table 4.

Table 3 — Presentation of the Statistical Results of In field demonstration of equivalence

	AM		**RM**	
Systematic deviation				
Grand averages	$\overline{\overline{x}}$	value	$\overline{\overline{z}}$	value
Repeatability				
Repeatability standard deviation	$s_r\left(\overline{\overline{x}}\right)$	value	$s_r\left(\overline{\overline{z}}\right)$	value
Variance of repeatability	$s_r^2\left(\overline{\overline{x}}\right)$	value	$s_r^2\left(\overline{\overline{z}}\right)$	value
Total number of measurements	N	value	N	value
			$s_{r,\text{limit}}\left(z\right)$	equation
			$s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$	value
			$s_R\left(z\right)$	equation
			$s_R\left(\overline{\overline{z}}\right)$	value
			$\dfrac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}}$	value
	$s\left(\overline{\overline{x}}\right)$	value	$s\left(\overline{\overline{z}}\right)$	value
			$C_1 = \dfrac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}$	value
			$C_0 = \overline{\overline{x}} - \dfrac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}\overline{\overline{z}}$	value

Table 4 — Compliance with the criteria

Verification tests	**Value obtained**		**Criterion**	**Conclusion** (result acceptable)
Systematic deviation				
correlation coefficient	r	value	$r \geq 0,97$	yes/no
slope	C_1	value	$1-\frac{s_R\left(\bar{\bar{z}}\right)}{\bar{\bar{z}}} \leq C_1 \leq 1+\frac{s_R\left(\bar{\bar{z}}\right)}{\bar{\bar{z}}}$	yes/no
intercept	C_0	value	$\lvert C_0 \rvert \leq s_R\left(\bar{\bar{z}}\right)$	yes/no
Repeatability standard deviation				
	$s_r\left(\bar{\bar{z}}\right)$ $s_r\left(\bar{\bar{x}}\right)$	value value	$s_r\left(\bar{\bar{z}}\right) \leq s_{r,\text{limit}}\left(\bar{\bar{z}}\right)$ $s_r\left(\bar{\bar{x}}\right) \leq s_{r,\text{limit}}\left(\bar{\bar{z}}\right)$	yes/no

The report shall include a general conclusion in which the laboratory shall state whether the method is acceptable.

It is presumed that for a method that is in the validation process, there is no aberrance. In fact, a method that has reached this stage shall already be statistically mastered and any deviations shall have been corrected. However, if for reasons left at the initiative of the person responsible for the validation, certain data shall be eliminated, this shall be mentioned and justified in the report.

Annex A
(informative)

Example of comparison of repeatability and trueness of Thorin Method and Ion Chromatography Method for SO_2 measurement in stack

This example provides data to check repeatability and trueness of the Thorin Method compared to those of the Ion Chromatography Method. The calculations according to EN 14793:2017 have been realized considering in one hand that the Ion Chromatography was the RM and in the second hand that the Thorin method was the AM and vice versa. Paired measurements ($n_i = 2$) have been performed simultaneously for the RM and the AM at each test i. Table A.1 to Table A.8 were set up according to the rules given in EN 14793:2017. All concentrations in the tables are expressed in mg/m^3.

Table A.1 — Ion Chromatography

Test	Parallel measurements		Number of measure-ments	Mean		Difference	Variance
i	z_{i1}	z_{i2}	n_i	$\overline{z}_i$	$\left(\overline{z}_i - \overline{\overline{z}}\right)^2$	$\left(z_{i1} - z_{i2}\right)$	$s^2\left(\overline{z}_i\right)$
1	43,81	46,32	2	45,07	237,95	−2,510	3,150
2	33,84	36,26	2	35,05	647,22	−2,420	2,928
3	65,68	67,71	2	66,70	38,50	−2,030	2,060
4	97,30	99,32	2	98,31	1430,32	−2,020	2,040
5	203,72	211,26	2	207,49	21608,86	−7,540	28,426
6	130,40	134,95	2	132,68	5210,61	−4,550	10,351
7	57,07	58,64	2	57,86	6,95	−1,570	1,232
8	165,67	176,66	2	171,17	12248,85	−10,990	60,390
9	104,35	110,25	2	107,30	2191,13	−5,900	17,405
10	42,40	43,85	2	43,13	301,56	−1,450	1,051
11	89,26	88,62	2	88,94	809,38	0,640	0,205
12	87,16	86,56	2	86,86	695,35	0,600	0,180
13	51,93	55,01	2	53,47	49,29	−3,080	4,743
14	22,37	22,59	2	22,48	1444,80	−0,220	0,024
15	108,73	108,82	2	108,78	2331,40	−0,090	0,004
16	133,55	139,72	2	136,64	5797,99	−6,170	19,034
17	92,64	97,74	2	95,19	1204,06	−5,100	13,005
18	51,65	55,71	2	53,68	46,38	−4,060	8,242
19	143,31	146,64	2	144,98	7137,64	−3,330	5,544
20	73,75	75,22	2	74,49	195,85	−1,470	1,080
21	38,90	39,56	2	39,23	452,01	−0,660	0,218
22	21,50	21,80	2	21,65	1508,58	−0,300	0,045
23	4,20	3,80	2	4,00	3191,17	0,400	0,080
24	3,50	3,20	2	3,35	3265,03	0,300	0,045
25	2,00	1,80	2	1,90	3432,84	0,200	0,020

26	1,40	1,30	2	1,35	3497,60	0,100	0,005
27	1,30	1,20	2	1,25	3509,43	0,100	0,005
28	5,80	5,30	2	5,55	3018,46	0,500	0,125
29	6,80	6,30	2	6,55	2909,57	0,500	0,125
30	8,70	8,00	2	8,35	2718,63	0,700	0,245
31	10,00	9,30	2	9,65	2584,75	0,700	0,245
32	3,79	1,50	2	2,65	3346,10	2,290	2,622
			N	$\bar{\bar{z}}$	$\text{SSD}\left(\bar{\bar{z}}\right)$	$s^2\left(\bar{\bar{z}}\right)$	$s_r^2\left(\bar{\bar{z}}\right)$
			64	60,49	97068,23	3131,23	5,777

The difference between the two values of the 32nd couple seems to be important. Therefore, an outlier test has been carried out (see Table A.2).

Table A.2 — Ion Chromatography – detection of outliers

Test	**Parallel measurements**		**Outlier test**		
i	z_{i1}	z_{i2}	$dz_i = \left(z_{i1} - z_{i2}\right)$	$e_i = \frac{dz_i}{\bar{z}_i}$	G_i
1	43,81	46,32	−2,51	−0,0557	0,51
2	33,84	36,26	−2,42	−0,0690	0,60
3	65,68	67,71	−2,03	−0,0304	0,36
4	97,30	99,32	−2,02	−0,0205	0,30
5	203,72	211,26	−7,54	−0,0363	0,40
6	130,40	134,95	−4,55	−0,0343	0,38
7	57,07	58,64	−1,57	−0,0271	0,34
8	165,67	176,66	−10,99	−0,0642	0,57
9	104,35	110,25	−5,90	−0,0550	0,51
10	42,40	43,85	−1,45	−0,0336	0,38
11	89,26	88,62	0,64	0,0072	0,13
12	87,16	86,56	0,60	0,0069	0,13
13	51,93	55,01	−3,08	−0,0576	0,53
14	22,37	22,59	−0,22	−0,0098	0,23
15	108,73	108,82	−0,09	−0,0008	0,18
16	133,55	139,72	−6,17	−0,0452	0,45
17	92,64	97,74	−5,10	−0,0536	0,50
18	51,65	55,71	−4,06	−0,0756	0,64
19	143,31	146,64	−3,33	−0,0230	0,31

20	73,75	75,22	−1,47	−0,0197	0,29
21	38,90	39,56	−0,66	−0,0168	0,28
22	21,50	21,80	−0,30	−0,0139	0,26
23	4,20	3,80	0,40	0,1000	0,44
24	3,50	3,20	0,30	0,0896	0,37
25	2,00	1,80	0,20	0,1053	0,47
26	1,40	1,30	0,10	0,0741	0,28
27	1,30	1,20	0,10	0,0800	0,32
28	5,80	5,30	0,50	0,0901	0,38
29	6,80	6,30	0,50	0,0763	0,29
30	8,70	8,00	0,70	0,0838	0,34
31	10,00	9,30	0,70	0,0725	0,27
32	3,79	1,50	2,29	0,8658	**5,13**
			$\overline{e}$	0,0284	
			$s(e_i)$	0,1634	

The critical value given by the Grubbs Table for n = 2 is 2,822. All values G_i are lower than the critical value, except for the 32nd couple of points that has to be withdrawn.

Table A.3 — Thorin method

Test	**Parallel measurements**		**Number of measurements**	**Mean**		**Difference**	**Variance**
i	x_{i1}	x_{i2}	n_i	$\overline{x}_i$	$\left(\overline{x}_i - \overline{\overline{x}}\right)^2$	$\left(x_{i1} - x_{i2}\right)$	$s^2\left(\overline{x}_i\right)$
1	45,54	49,64	2	47,59	216,12	−4,100	8,405
2	36,08	38,61	2	37,35	622,31	−2,530	3,200
3	67,80	69,90	2	68,85	43,02	−2,100	2,205
4	99,56	101,36	2	100,46	1456,87	−1,800	1,620
5	205,57	213,09	2	209,33	21620,44	−7,520	28,275
6	132,62	136,77	2	134,70	5242,33	−4,150	8,611
7	59,66	60,45	2	60,06	5,00	−0,790	0,312
8	173,04	180,16	2	176,60	13066,53	−7,120	25,347
9	109,41	113,97	2	111,69	2440,25	−4,560	10,397
10	45,77	47,77	2	46,77	240,90	−2,000	2,000
11	93,63	95,25	2	94,44	1033,55	−1,620	1,312
12	88,85	89,09	2	88,97	711,76	−0,240	0,029

13	55,47	58,38	2	56,93	28,79	−2,910	4,234
14	24,70	26,44	2	25,57	1348,44	−1,740	1,514
15	109,29	112,21	2	110,75	2348,27	−2,920	4,263
16	136,94	150,22	2	143,58	6607,89	−13,280	88,179
17	95,89	104,69	2	100,29	1443,92	−8,800	38,720
18	54,84	59,15	2	57,00	28,05	−4,310	9,288
19	114,65	147,19	2	130,92	4709,93	−32,540	529,426
20	60,37	66,65	2	63,51	1,49	−6,280	19,719
21	33,54	36,70	2	35,12	738,27	−3,160	4,993
22	20,12	21,40	2	20,76	1724,83	−1,280	0,819
23	6,70	6,10	2	6,40	3123,81	0,600	0,180
24	5,00	4,60	2	4,80	3305,23	0,400	0,080
25	4,30	3,90	2	4,10	3386,20	0,400	0,080
26	4,20	3,90	2	4,05	3392,03	0,300	0,045
27	4,20	3,90	2	4,05	3392,03	0,300	0,045
28	9,80	9,10	2	9,45	2792,18	0,700	0,245
29	8,70	8,10	2	8,40	2904,25	0,600	0,180
30	11,20	10,40	2	10,80	2651,33	0,800	0,320
31	11,10	10,40	2	10,75	2656,48	0,700	0,245
32	9,60	9,00	2	9,30	2808,06	0,600	0,180
			N	$\overline{\overline{x}}$	$\mathrm{SSD}\left(\overline{\overline{x}}\right)$	$s^2\left(\overline{\overline{x}}\right)$	$s_r^2\left(\overline{\overline{x}}\right)$
			64	62,29	96090,54	3099,69	24,827

The difference between the two values of the 19th couple seems to be important. Therefore, an outlier test has been carried out (see Table A.4).

Table A.4 — Thorin method– detection of outliers

Test	**Parallel measurements**		**Outlier test**		
i	z_{i1}	z_{i2}	$\mathrm{d}z_i = \left(z_{i1} - z_{i2}\right)$	$e_i = \frac{\mathrm{d}z_i}{\overline{z}_i}$	G_i
1	45,54	49,64	−4,10	−0,0862	0,89
2	36,08	38,61	−2,53	−0,0677	0,65
3	67,80	69,90	−2,10	−0,0305	0,17
4	99,56	101,36	−1,80	−0,0179	0,01
5	205,57	213,09	−7,52	−0,0359	0,24
6	132,62	136,77	−4,15	−0,0308	0,17

7	59,66	60,45	−0,79	−0,0132	0,05
8	173,04	180,16	−7,12	−0,0403	0,30
9	109,41	113,97	−4,56	−0,0408	0,30
10	45,77	47,77	−2,00	−0,0428	0,33
11	93,63	95,25	−1,62	−0,0172	0,00
12	88,85	89,09	−0,24	−0,0027	0,19
13	55,47	58,38	−2,91	−0,0511	0,44
14	24,70	26,44	−1,74	−0,0680	0,66
15	109,29	112,21	−2,92	−0,0264	0,12
16	136,94	150,22	−13,28	−0,0925	0,97
17	95,89	104,69	−8,80	−0,0877	0,91
18	54,84	59,15	−4,31	−0,0756	0,75
19	114,65	147,19	−32,54	−0,2485	**2,99**
20	60,37	66,65	−6,28	−0,0989	1,05
21	33,54	36,70	−3,16	−0,0900	0,94
22	20,12	21,40	−1,28	−0,0617	0,57
23	6,70	6,10	0,60	0,0938	1,44
24	5,00	4,60	0,40	0,0833	1,30
25	4,30	3,90	0,40	0,0976	1,48
26	4,20	3,90	0,30	0,0741	1,18
27	4,20	3,90	0,30	0,0741	1,18
28	9,80	9,10	0,70	0,0741	1,18
29	8,70	8,10	0,60	0,0714	1,15
30	11,20	10,40	0,80	0,0741	1,18
31	11,10	10,40	0,70	0,0651	1,07
32	9,60	9,00	0,60	0,0645	1,06
			$\overline{e}$	−0,0173	
			$s(e_i)$	0,0774	

The critical value given by the Grubbs Table for n = 2 is 2,822. All values G_i are lower than the critical value, except for the 19th couple of points that has to be withdrawn.

Table A.5 — Ion Chromatography (19th and 32nd couples skipped)

Test	Parallel measurements		Number of measurements	Mean		Difference	Variance
i	z_{i1}	z_{i2}	n_i	$\overline{z}_i$	$\left(\overline{z}_i-\overline{\overline{z}}\right)^2$	$\left(z_{i1}-z_{i2}\right)$	$s^2\left(\overline{z}_i\right)$
1	43,81	46,32	2	45,07	237,95	−2,510	3,150
2	33,84	36,26	2	35,05	647,22	−2,420	2,928
3	65,68	67,71	2	66,70	38,50	−2,030	2,060
4	97,30	99,32	2	98,31	1430,32	−2,020	2,040
5	203,72	211,26	2	207,49	21608,86	−7,540	28,426
6	130,40	134,95	2	132,68	5210,61	−4,550	10,351
7	57,07	58,64	2	57,86	6,95	−1,570	1,232
8	165,67	176,66	2	171,17	12248,85	−10,990	60,390
9	104,35	110,25	2	107,30	2191,13	−5,900	17,405
10	42,40	43,85	2	43,13	301,56	−1,450	1,051
11	89,26	88,62	2	88,94	809,38	0,640	0,205
12	87,16	86,56	2	86,86	695,35	0,600	0,180
13	51,93	55,01	2	53,47	49,29	−3,080	4,743
14	22,37	22,59	2	22,48	1444,80	−0,220	0,024
15	108,73	108,82	2	108,78	2331,40	−0,090	0,004
16	133,55	139,72	2	136,64	5797,99	−6,170	19,034
17	92,64	97,74	2	95,19	1204,06	−5,100	13,005
18	51,65	55,71	2	53,68	46,38	−4,060	8,242
20	73,75	75,22	2	74,49	195,85	−1,470	1,080
21	38,90	39,56	2	39,23	452,01	−0,660	0,218
22	21,50	21,80	2	21,65	1508,58	−0,300	0,045
23	4,20	3,80	2	4,00	3191,17	0,400	0,080
24	3,50	3,20	2	3,35	3265,03	0,300	0,045
25	2,00	1,80	2	1,90	3432,84	0,200	0,020
26	1,40	1,30	2	1,35	3497,60	0,100	0,005
27	1,30	1,20	2	1,25	3509,43	0,100	0,005
28	5,80	5,30	2	5,55	3018,46	0,500	0,125
29	6,80	6,30	2	6,55	2909,57	0,500	0,125
30	8,70	8,00	2	8,35	2718,63	0,700	0,245

31	10,00	9,30	2	9,65	2584,75	0,700	0,245
			N	$\bar{\bar{z}}$	$\mathrm{SSD}\left(\bar{\bar{z}}\right)$	$s^2\left(\bar{\bar{z}}\right)$	$s_r^2\left(\bar{\bar{z}}\right)$
			60	59,60	86560,84	2984,86	5,890

Table A.6 — Thorin method (19th and 32nd couples skipped)

Test	**Parallel measurements**		**Number of measurements**	**Mean**		**Difference**	**Variance**
i	x_{i1}	x_{i2}	n_i	$\bar{x}_i$	$\left(\bar{x}_i - \bar{\bar{x}}\right)^2$	$\left(x_{i1} - x_{i2}\right)$	$s^2\left(\bar{x}_i\right)$
1	45,54	49,64	2	47,59	216,12	−4,100	8,405
2	36,08	38,61	2	37,35	622,31	−2,530	3,200
3	67,80	69,90	2	68,85	43,02	−2,100	2,205
4	99,56	101,36	2	100,46	1456,87	−1,800	1,620
5	205,57	213,09	2	209,33	21620,44	−7,520	28,275
6	132,62	136,77	2	134,70	5242,33	−4,150	8,611
7	59,66	60,45	2	60,06	5,00	−0,790	0,312
8	173,04	180,16	2	176,60	13066,53	−7,120	25,347
9	109,41	113,97	2	111,69	2440,25	−4,560	10,397
10	45,77	47,77	2	46,77	240,90	−2,000	2,000
11	93,63	95,25	2	94,44	1033,55	−1,620	1,312
12	88,85	89,09	2	88,97	711,76	−0,240	0,029
13	55,47	58,38	2	56,93	28,79	−2,910	4,234
14	24,70	26,44	2	25,57	1348,44	−1,740	1,514
15	109,29	112,21	2	110,75	2348,27	−2,920	4,263
16	136,94	150,22	2	143,58	6607,89	−13,280	88,179
17	95,89	104,69	2	100,29	1443,92	−8,800	38,720
18	54,84	59,15	2	57,00	28,05	−4,310	9,288
20	60,37	66,65	2	63,51	1,49	−6,280	19,719
21	33,54	36,70	2	35,12	738,27	−3,160	4,993
22	20,12	21,40	2	20,76	1724,83	−1,280	0,819
23	6,70	6,10	2	6,40	3123,81	0,600	0,180
24	5,00	4,60	2	4,80	3305,23	0,400	0,080
25	4,30	3,90	2	4,10	3386,20	0,400	0,080
26	4,20	3,90	2	4,05	3392,03	0,300	0,045

27	4,20	3,90	2	4,05	3392,03	0,300	0,045
28	9,80	9,10	2	9,45	2792,18	0,700	0,245
29	8,70	8,10	2	8,40	2904,25	0,600	0,180
30	11,20	10,40	2	10,80	2651,33	0,800	0,320
31	11,10	10,40	2	10,75	2656,48	0,700	0,245
			N	$\overline{\overline{x}}$	$\text{SSD}\left(\overline{\overline{x}}\right)$	$s^2\left(\overline{\overline{x}}\right)$	$s_r^2\left(\overline{\overline{x}}\right)$
			60	61,77	88564,41	3053,95	8,829

The data presented in Table A.5 and Table A.6 have been evaluated by the procedure described in EN 15267-4:2017 to demonstrate the equivalence between an Alternative Method with a Reference Method. The statistical results and conclusions are presented in Table A.7 and Table A.8 for the Ion Chromatography Method as the RM and the Thorin Method as the AM and vice versa.

Table A.7 — Presentation of the statistical results of infield demonstration of equivalence

	Thorin Method		**Ion Chromatography Method**	
Systematic deviation				
Grand averages	$\overline{\overline{x}}$	61,77	$\overline{\overline{z}}$	59,60
Repeatability				
Repeatability standard deviation	$s_r\left(\overline{\overline{x}}\right)$	2,971	$s_r\left(\overline{\overline{z}}\right)$	2,427
Variance of repeatability	$s_r^2\left(\overline{\overline{x}}\right)$	8,829	$s_r^2\left(\overline{\overline{z}}\right)$	5,890
Total number of measurements	N	60	N	60
	$s_{r,\text{limit}}\left(x\right)$	0,051 x + 2,3	$s_{r,\text{limit}}\left(z\right)$	0,051 z +2,3
	$s_{r,\text{limit}}\left(\overline{\overline{x}}\right)$	5,45	$s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$	5,34
	$s_R\left(x\right)$	0,0841 x – 0,8086	$s_R\left(z\right)$	0,0678 z + 3,47
	$s_R\left(\overline{\overline{x}}\right)$	4,39	$s_R\left(\overline{\overline{z}}\right)$	7,51
	$\dfrac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}}$	0,071	$\dfrac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}}$	0,126
	$s\left(\overline{\overline{x}}\right)$	55,26	$s\left(\overline{\overline{z}}\right)$	54,63
	$C_1 = \dfrac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}$	1,0115	$C_1^{'} = \dfrac{s(\overline{\overline{z}})}{s\left(\overline{\overline{x}}\right)}$	0,9885
	$C_0 = \overline{\overline{x}} - \dfrac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}\overline{\overline{z}}$	1,48	$C_0^{'} = \overline{\overline{z}} - \dfrac{s\left(\overline{\overline{z}}\right)}{s\left(\overline{\overline{x}}\right)}\overline{\overline{x}}$	−1,46

Table A.8 — Compliance with the criteria

Verification tests	**Value obtained**		**Criterion**	**Conclusion** (results acceptable)
Systematic deviation				
correlation coefficient	r	0,9984	$r \geq 0{,}97$	yes
slope	C_1	1,0115	$1-\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}} \leq C_1 \leq 1+\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}}$ $0{,}874 \leq C_1 \leq 1{,}126$	yes
	$C_1^{'}$	0,9885	$1-\frac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}} \leq C_1{'} \leq 1+\frac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}}$ $0{,}929 \leq C_1 \leq 1{,}071$	yes
intercept	C_0	1,48	$\lvert C_0 \rvert \leq s_R\left(\overline{\overline{z}}\right)$ $\lvert C_0 \rvert \leq 7{,}51$	yes
	$C_0^{'}$	−1,46	$\lvert C_0{'} \rvert \leq s_R\left(\overline{\overline{x}}\right)$ $\lvert C_0{'} \rvert \leq 4{,}39$	yes
Repeatability standard deviation				
	$s_r\left(\overline{\overline{z}}\right)$	2,43 < 5,34	$s_r\left(\overline{\overline{z}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$	yes
	$s_r\left(\overline{\overline{x}}\right)$	2,97 < 5,45	$s_r\left(\overline{\overline{x}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{x}}\right)$	yes

Calculations considering in one hand that the RM was the Ion Chromatography and in the second hand that the Thorin method lead to the same conclusions: both methods are equivalent.

Annex B
(informative)

Critical values for Grubbs test

Table B.1 shows critical values for Grubbs test which correspond to a level of risk, namely α = 5 %

Table B.1 — Critical values for Grubbs test

Number of trials	Critical value
15	2,549
16	2,585
17	2,620
18	2,651
19	2,681
20	2,709
21	2,733
22	2,758
23	2,781
24	2,802
25	2,822
26	2,841
27	2,859
28	2,876
29	2,893
30	2,908
35	2,979
40	3,036
50	3,146

Annex C
(normative)

Minimum requirements for a test bench

The generation mode of the testing bench should be able to provide matrices of gases and the relevant concentration levels with regard to the actual conditions encountered on industrial site and ELV. The gas shall be issued in the testing bench at levels of temperature and humidity corresponding to actual conditions. Indeed it should be recalled that the major source of uncertainty in an emission measurement method is the sampling part and that it shall be implemented in the conditions as close as possible to the conditions of site.

It is also necessary to ensure that the generation period is in line with the minimum sampling duration provided in the standards describing measuring methods;

Comparison of measuring devices shall be carried out at measurements points where the equivalence of the concentrations of the parameters to be measured has been demonstrated.

The body organizing the inter-comparisons of methods on its test bench shall have the necessary competence.

NOTE The test bench provider can demonstrate the necessary competence e.g. by accreditation on the basis of EN ISO/IEC 17043.

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