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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 It supersedes DD CEN/TS 14793:2005 which is withdrawn.

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English Version

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

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of an identical text or by endorsement, at the latest by July 2017, and conflicting national standards shall be withdrawn at the latest by July 2017.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 interferences.

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	$C_0 = \bar{\bar{x}} - \frac{s(\bar{\bar{x}})}{s(\bar{\bar{z}})} \bar{\bar{z}}$
C_1	slope of the orthogonal regression line between AM and RM values	$C_1 = \frac{s(\bar{\bar{x}})}{s(\bar{\bar{z}})}$
dx_i	difference between x_{i1} and x_{i2} for each value of i	$dx_i = (x_{i1} - x_{i2})$
e_i	ratio between dx_i and $\bar{x}_i$ for each value of i	$e_i = \frac{dx_i}{\bar{x}_i}$
$\bar{e}$	average value of the values e_i	$\bar{e} = \frac{\sum_{i=1}^n e_i}{n}$
G_i	ratio between $(e_i - \bar{e})$ and $s(e_i)$	$G_i = \frac{ e_i - \bar{e} }{s(e_i)}$
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	$r = \frac{SPD(\bar{\bar{x}}, \bar{\bar{z}})}{\sqrt{SSD(\bar{\bar{x}}) \times SSD(\bar{\bar{z}})}}$
$s(e_i)$	standard deviation of the population of the e_i	$s(e_i) = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (e_i - \bar{e})^2}$
$s^2(\bar{\bar{x}})$	variance of the AM	$s^2(\bar{\bar{x}}) = \frac{SSD(\bar{\bar{x}})}{p-1}$
$s_r(\bar{\bar{x}})$	repeatability standard deviation of the AM	

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