SLOVENSKI STANDARD
SIST-TS CEN/TS 14793:2005

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Emisije nepremiļ nih virov ï Notranji laboratorijski postopki validacije alternativne metode v primerjavi z referenļ no metodo

Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method

Emissionen aus stationären Quellen - Laborinterne Validierung von Alternativverfahren durch Vergleich mit einem Referenzverfahren

Emissions de sources fixes - Méthode de validation intralaboratoire d'une méthode 'alternative' comparée a une méthode de référence

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English version

Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method

Emissions de sources fixes - Méthode de validation intralaboratoire d'une méthode 'alternative' comparée à une méthode de référence

Emissionen aus stationären Quellen - Intralaborvalidierverfahren für ein Alternativverfahren verglichen mit einem Referenzverfahren

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Foreword

This document CEN/TS 14793:2005 has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Annexes A and B are informative.

Introduction

Much has been published in the literature concerning method validation by collaborative study. CEN TC264 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 may be esoteric to the extent that no other laboratories would be interested in collaboration. Those that might be interested can be competitors.

The present Technical Specification provides one of the possible methods of testing the equivalence of an alternative method with a reference method.

1 Scope

The purpose of this Technical Specification is to specify a validation procedure to show if an Alternative Method (AM) can be used as an alternative to the Standard Reference Method (SRM), both implemented to determine the same measurand. This document has been drawn up for laboratories working in air pollution measurements (and consequently examples taken from this sector are included in the appendices).

In particular, this Technical Specification provides the statistical tools and different criteria to evaluate the alternative method; this does not release the person responsible for this validation from bearing technical and analytical judgement on the evaluation of the different criteria.

Three steps are described in the validation procedure:

— description of the AM and setting of the field of equivalence (range and type of gas matrix);

— determination of the performance characteristics of the AM and calculation of the overall uncertainty where appropriate and check of compliance of the maximum overall uncertainty allowed for the SRM;

— check of repeatability and lack of systematic deviation of the AM in the field in comparison with the SRM for the type of matrix defined in the field of equivalence.

NOTE Some parts of the second step of the validation of the alternative method should be performed by a recognised test-house.

If the AM fulfils the requirement of the procedure, then the laboratory that carried out the whole validation process is allowed to use it as a SRM in the field application where the equivalence has been demonstrated.

However, if the validation process involves at least 4 different accredited laboratories performing simultaneously parallel measurements in the field, and if the AM passes with success all the tests of the procedure, then this method could be proposed to CEN, who can decide to consider this AM as a new reference method (ARM).

The use of this procedure implies that a reference method has been defined by the regulator or in a contract and has been validated.

This Technical Specification only considers the case of linear quantitative methods.

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.

ENV 13005, *Guide to the expression of uncertainly in measurement.*

EN ISO 14956, *Air quality – Evaluation of suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002).*

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.*

3 Terms and definitions

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

3.1 General Vocabulary

3.1.1
accepted reference value (see ENV 13005)
value which serves as an accepted reference value (or conventionally true value) of the sample, provided by the arithmetic mean of the measurement values repeated according to the standard reference method (see 3.1.19)

3.1.2
alternative method (AM)
measurement method (3.1.15) which complies with the criteria given by this Technical Specification with respect to the reference method (SRM)

NOTE An alternative analysis method can consist of a simplification of the reference method.

3.1.3
automatic measuring system (AMS)
measuring system interacting with one or several air quality characteristics and which returns an output signal giving the measurement result expressed in the physical unit of such air quality characteristics

3.1.4
calibration
set of operations that establishes, under specified conditions, the systematic difference that may exist between values of a measurand indicated by a measuring system and the corresponding values given by a "reference" system represented by the reference materials and their accepted values (derived from VIM 6.11 and from ISO 11095:1996, clause 4)

NOTE 1 The result of a calibration permits either the assignment of values of the measurand to the indications or the determination of corrections with respect to indications.

NOTE 2 A calibration may also determine other metrological properties such as the effect of influence quantities.

3.1.5
field of application of the measurement method
combination of the different types of matrix (3.1.12) and the range of concentrations of the measurand (3.1.14) covered, to which the measurement method (3.1.15) is applied

NOTE 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.

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. Multi-component measurement methods like FTIR).

WARNING 2 The definition of the field of application depends entirely upon the laboratory responsible for the validation study 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.

3.1.6
field repeatability conditions
the conditions in which independent test results are obtained by one laboratory using the same method carried out through two measurement systems set up according a written procedure and measuring simultaneously the concentration of the measurand

[ISO 5725-1:1994]

3.1.7
field reproducibility conditions
the conditions in which independent test results are obtained by at least two laboratories using the same method carried out through two measurement systems set up according a written procedure and measuring simultaneously the concentration of the measurand

[ISO 5725-1:1994]

3.1.8
lack of fit
systematic deviation within the range of application between the measurement result obtained by applying the linear model equation to the observed response of the measuring system measuring reference materials and the corresponding accepted value of such reference materials

NOTE 1 Lack of fit may be a function of the measurement result.

NOTE 2 Since bias is considered as too specific and to difficult to be determined experimentally, the concept of lack of fit is selected for this Technical Specification.

3.1.9
limit of detection (L_D)
smallest measurand (3.1.14) concentration which can be detected, but not quantified, in the experiment conditions described for the method

3.1.10
limit of quantification (L_Q)
smallest measurand (3.1.14) concentration which can be quantified, in the experiment conditions described for the method

3.1.11
linearity
capacity of a measurement method (3.1.15), within certain limits, to provide an instrument response or results proportional to the quantity of the measurand (3.1.14) to be determined in the sample

This proportionality is expressed through a defined a priori mathematical expression.

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.

3.1.12
matrix
all the components of the sample other than the measurand (3.1.14) that could influence the measurement

3.1.13
maximum permissible errors
extreme values of the error permitted by specifications, regulations, etc. for the given measuring system (VIM:1994, 5.21)

3.1.14
measurand
subject that is characterised by a measurement method (3.1.15)

3.1.15
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, reagents, equipment, procedures, presentation of results, repeatability (3.1.16) and other requirements, test report

3.1.16
repeatability
the closeness of agreement between independent test results obtained in the stipulated conditions

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

NOTE 2 The measurement 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 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.

[ISO 5725-1:1994]

3.1.17
standard deviation of field repeatability
standard repeatability of numerous repetitions obtained by a laboratory in field repeatability conditions (see 3.1.6)

3.1.18
standard deviation of field reproducibility
standard reproducibility of numerous repetitions obtained by at least two laboratories in field reproducibility conditions (see 3.1.7)

3.1.19
standardised reference method (SRM)
measurement method (3.1.15) recognised by experts and taken as a reference by convention, which gives, or is presumed to give, the accepted reference value of the concentration of the measurand (3.1.14) to be measured

3.1.20
trueness
closeness of agreement between the mean value obtained from a large series of test results and an accepted reference value

[ISO 5725-1:1994]

NOTE 1 The measurement of trueness is generally expressed in terms of a bias or a systematic deviation.

3.1.21
validation of a measurement method
act of subjecting a measurement method (3.1.15) 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 In the framework of this Technical Specification, the validation of a method is mainly based on an “in field” study that includes comparison to a reference method.

3.2 Symbols

For the requirements of this Technical Specification, the symbols and notations defined in Table 1 are applicable.

Table 1 – Symbols

Symbol	Description
C_0	Intercept of the orthogonal regression line between AM and SRM values
C_1	Slope of the orthogonal regression line between AM and SRM values
dx_i	Difference between x_{i1} and x_{i2} for each value of i
e_i	Relative value e_i of ratio between dx_i and x_{iav} for each value of i,
G_i	Ratio between $\left(e_i - \bar{e}\right)$ and s_{ei}
L_D	Limit of detection
L_Q	Limit of quantification
p	Number of trials
n_i	Number of parallel measurement for the alternative method
m_i	Number of parallel measurement for the reference method
s_{ei}	Standard deviation of the population of the e_i
$s_r(x)$	Standard deviation of repeatability for the alternative method
$s_r(z)$	Standard deviation of repeatability for the reference method
$S_{r\ limit}(z)$	Maximum allowable standard deviation of repeatability for the reference method
$s_R(x)$	Standard deviation of reproducibility for the alternative method
$s_R(z)$	Standard deviation of reproducibility for the reference method
u_{cSRM}	Maximum combined standard uncertainty given in the SRM standard
x_{ij}	Measurement of the concentration obtained by the alternative method for a trial *i* and repetition *j*
x_p	Outlier
x_{iav}	Average value for each value of i
z_{ij}	Measurement of the concentration obtained by the reference method for a trial *i* and repetition *j*

Table 1 (*concluded*)

Symbol	Description	Formula
$\bar{x}_j$	Arithmetic mean of a variable x for which n_i measurements have been taken	$\bar{x}_j = \dfrac{\sum_{i=1}^{n_i} x_{ij}}{n_i}$
$\bar{\bar{x}}$	Grand average of a variable x for which N measurements have been taken	$\bar{\bar{x}} = \dfrac{\sum_{i=1}^{p}\sum_{j=1}^{n_i} x_{ij}}{N}$
$N(x)$	Total number of measurements for AM	$N(x) = \sum_{i=1}^{p} n_i$
$N(z)$	Total number of measurements for SRM	$N(z) = \sum_{i=1}^{p} m_i$
$SSD(\bar{x})$	Sum of the squares of the mean deviations for a variable x	$SSD(\bar{x}) = \sum_{i=1}^{p} \bar{x}_i^2 - \dfrac{\left(\sum_{i=1}^{p} \bar{x}_i\right)^2}{p}$
$s^2(\bar{x})$	Variance of a variable $\bar{x}$	$s^2(\bar{x}) = \dfrac{SSD(\bar{x})}{p-1}$
$s_r^2(x)$	Repeatability variance of the alternative method	$s_r^2(x) = \dfrac{\sum_{i=1}^{p}\sum_{j=1}^{n_i}(x_{ij} - \bar{x}_i)^2}{N(x) - p}$
k	Coefficient of the orthogonal regression line	$k = t_{1-\alpha/2}^2 \dfrac{1-r^2}{n-2}$
r	Regression coefficient	$r = \dfrac{SPD(\bar{x},\bar{z})}{\sqrt{SSD(\bar{x}).SSD(\bar{z})}}$
$SPD(\bar{x},\bar{z})$	Sum of the products of the deviations for two variables $\bar{x}$ and $\bar{z}$	$SPD(\bar{x},\bar{z}) = \sum_{i=1}^{p} \bar{x}_i \bar{y}_i - \dfrac{\sum_{i=1}^{p} \bar{x}_i \sum_{i=1}^{p} \bar{y}_i}{p}$