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Analize jekla in železa - Mednarodni laboratorijski postopek za preverjanje ujemanja v analizni metodi z uporabo certificiranih referenčnih materialov

Analysis of steels and irons - Internal laboratory procedure for checking the accuracy of an analytical method by using Certified Reference Materials

Analyse von Stahl und Eisen - Laboratoriumsinternes Verfahren zur Überprüfung der Richtigkeit eines - Analysenverfahrens mit Hilfe zertifizierter Referenzmaterialien

Analyse des aciers et des fontes - Méthodes de contrôle intralaboratoire de l'exactitude d'une procédure analytique au moyen de Matériaux de Référence Certifiés

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Analysis of steels and irons - Internal laboratory procedure for checking the accuracy of an analytical method by using Certified Reference Materials

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Foreword

This document (CEN/TR 10350:2013) has been prepared by Technical Committee ECISS/TC 102 “Methods of chemical analysis for iron and steel”, the secretariat of which is held by SIS.

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

This document supersedes CEN/TR 10350:2009.

In comparison with the previous version of CEN/TR 10350, the following significant technical changes were made:

— Definition 3.12: Correction of the definition for “uncertainty of the certified values”;

— Table C.7: Correction of the confidence level for χ^2;

— C.2.3.3: Correction of the sample label: G instead of A.

Introduction

This Technical Report defines a procedure for checking, in each specific laboratory, the accuracy of an analytical method by the application of statistical principles to the analytical results obtained on Certified Reference Materials (CRMs).

This Technical Report is an adaptation of ISO Guide 33:2000 mostly for the specific cases where EURONORM-CRMs are used for checking, in an intralaboratory context, the accuracy of an analytical method.

Nevertheless, it may be adopted in any other case where CRMs selected have similar quality levels to those of EURONORM-CRMs.

1 Scope

The present statistical procedure describes how to check results for absence of bias by comparison of these analytical results with those obtained during the certification of CRMs.

If the resulting data confirm the absence of bias, the method may be considered accurate when applied to all steels and irons whose composition ranges are adequately covered or bounded by the CRMs used.

The resulting data give also an estimate of the repeatability and/or the intermediate precision ("intralaboratory reproducibility") for the CRMs used. The comparison of these analytical data with the repeatability data obtained during the certification may also be performed depending on the strict purpose of the method under consideration.

For the purpose of this Technical Report, the use of existing CRMs is essential for the assessment of the trueness, but it may be only indicative for the other statistical data.

NOTE This Technical Report does not describe the use of CRMs as calibrants, this subject being treated in ISO Guide 32.

2 Principle

This Technical Report describes a procedure for checking an analytical method used in a specific laboratory by using data obtained from the analysis of CRMs.

The absence of bias ascertained with CRMs can be extended to the trueness of further analytical samples adequately covered or bounded by the selected CRMs. Nevertheless it should be underlined that this Technical Report is not appropriate for the assessment of the repeatability and/or the intermediate precision data of the further analytical samples to be tested by the analytical method under consideration.

Checking the trueness of an analytical method as applied by a specific laboratory involves the comparison of the mean value of the analytical results obtained by using CRMs with the certified value of each CRM selected. The standard deviation of the intralaboratory means of the selected CRMs is taken into account when making this comparison. Moreover, adjustment values chosen in advance by the laboratory, according to economic or technical limitations or stipulations are also taken into account.

3 Terms and definitions

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

3.1
certified reference material
CRM
reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

NOTE 1 The concept of value includes qualitative attributes such as identity or sequence. Uncertainties for such attributes may be expressed as probabilities.

NOTE 2 Metrologically valid procedures for the production and certification of reference materials are given in, among others, ISO Guides 34 and 35.

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

NOTE 4 VIM has an analogous definition (ISO/IEC Guide 99:2007, 5.14).

[SOURCE: ISO Guide 30; Amendment 1:2008]

3.2
reference material
RM
material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

NOTE 1 RM is a generic term.

NOTE 2 Properties can be quantitative or qualitative, e.g. identity of substances or species.

NOTE 3 Uses may include the calibration of a measurement system, assessment of a measurement procedure, assigning values to other materials, and quality control.

NOTE 4 A single RM cannot be used for both calibration and validation of results in the same measurement procedure.

NOTE 5 VIM has an analogous definition (ISO/IEC Guide 99:2007, 5.13), but restricts the term “measurement” to apply to quantitative values and not to qualitative properties. However, NOTE 3 of ISO/IEC Guide 99:2007, 5.13, specifically includes the concept of qualitative attributes, called “nominal properties”.

[SOURCE: ISO Guide 30; Amendment 1:2008]

3.3
accuracy
closeness of agreement between a test result and the true value

NOTE 1 In practice, the accepted reference value is substituted for the true value.

NOTE 2 The term "accuracy", when applied to a set of test or measurement results, involves a combination of random components and common systematic error or bias component.

NOTE 3 Accuracy refers to a combination of trueness and precision.

[SOURCE: ISO 3534-2:2006, 3.3.1]

3.4
bias
difference between the expectation of a test result or a measurement result and a true value

NOTE 1 Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the true value is reflected by a larger bias value.

NOTE 2 The bias of a measuring instrument is normally estimated by averaging the error of indication over an appropriate number of repeated measurements. The error of indication is the "indication of a measuring instrument minus a true value of the corresponding input quantity".

NOTE 3 In practice, the accepted reference value is substituted for the true value.

[SOURCE: ISO 3534-2:2006, 3.3.2]

3.5
precision
closeness of agreement between independent test/measurement results obtained under stipulated conditions

NOTE 1 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

NOTE 3 Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[SOURCE: ISO 3534-2:2006, 3.3.4]

3.6
repeatability
precision under repeatability conditions

[SOURCE: ISO 3434-2:2006, 3.3.5]

3.7
repeatability conditions
conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in the same test or measuring facility by the same operator using the same equipment within short intervals of time

NOTE Repeatability conditions include:

a) the same measurement procedure or test procedure;

b) the same operator;

c) the same measuring or test equipment used under the same conditions;

d) the same location;

e) repetition over a short period of time.

[SOURCE: ISO 3434-2:2006, 3.3.6]

3.8
reproducibility
precision under reproducibility conditions

NOTE 1 Reproducibility can be expressed quantitatively in terms of the dispersion characteristics of the results.

NOTE 2 Results are usually understood to be corrected results.

NOTE 3 This definition is not used in the present document: it is given only to clarify the next item.

[SOURCE: ISO 3534-2:2006, 3.3.10]

3.9
reproducibility conditions
observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in different test or measurement facilities with different operators using different equipment

[SOURCE: ISO 3534-2:2006, 3.3.11]

3.10
intermediate precision
precision under intermediate precision conditions

[SOURCE: ISO 3534-2:2006, 3.3.15]

3.11
intermediate precision conditions
conditions where test results or measurement results are obtained with the same method, on identical test/measurement items in the same test or measurement facility, under some different operating condition

NOTE 1 There are four elements to the operating condition: time, calibration, operator and equipment.

NOTE 2 A test house is an example of a test facility. A metrology laboratory is an example of a measurement facility.

[SOURCE: ISO 3534-2:2006, 3.3.16]

3.12
uncertainty of the certified values
in the particular case of EURONORM-CRMs, the uncertainty of each certified value is expressed as the 95 % half-width confidence interval "C(95 %)" of the mean of the intralaboratory means

Note 1 to entry: It is calculated from Formula (1):

$$C(95\,\%) = \frac{t \times S_M}{\sqrt{n}} \qquad (1)$$

where

t is the Student's value at the desired probability with n-1 degrees of freedom;

S_M is the standard deviation of the intralaboratory means;

n is the number of acceptable intralaboratory mean values.

Note 2 to entry: This definition is not used in the present document; it is only given for clarification.

4 Procedure

4.1 General

The analytical method for the measurement shall be fixed, i.e. a written document shall exist laying down all the details. There shall be no changes to the method during the course of the experiment.

CRMs to be selected shall cover the range of the analytical method, which shall at least be bounded with low and high content, and if possible, shall include an intermediate content.

Furthermore, it should be possible to extend the choice of CRMs to cover similar matrices representing the compositions of the analytical samples intended to be analysed.

For example, if the analytical method concerns the determination of copper in low alloy steel samples with a nickel content of about 0,01 % and also in samples having a nickel content of about 1 % it is advisable to test the method within its full range for both kind of matrices.

4.2 Number of replicate determinations

The number of replicate determinations required, n_0, depends mainly on the values of α and β and the alternative hypothesis chosen for the assessment of the precision.

NOTE α is the significance level and β is the type II error probability.

Table 1 shows the relation between the degrees of freedom ν (where in this case $\nu = n - 1$) and the ratio of the within-laboratory standard deviation of the analytical method, σ_{W1}, and the required value of the within-laboratory standard deviation, σ_{W0}, for various values of β at $\alpha = 0,05$.

For example, for $n = 10$ the probability that the variance of the analytical results will pass the appropriate χ^2-test at $\alpha = 0,05$ is no more than 1 % when within-laboratory standard deviation, σ_{W1}, of the analytical method is equal or larger than 2,85 times the required value of σ_{W0}.

The user needs to establish, before the analysis, an appropriate level of acceptability with regard to the ratio of σ_{W1} to σ_{W0} (the null hypothesis) and also the probability of falsely accepting a method which has, in fact, unacceptable precision (β, which is also the type II error probability).

Assume therefore that a user has decided that a method is acceptable if the within laboratory standard deviation is not more than three times the certification standard deviation. This makes the null hypothesis $\sigma_{W1} \leq 3\,\sigma_{W0}$ and the alternative hypothesis $\sigma_{W1} > 3\,\sigma_{W0}$. Assume also that the user has decided that the acceptable probability of a false acceptance of the null hypothesis is 0,05 (or 5 %). From Table 1, reading down column 3 ($\beta = 0,05$), the first number less than 3 is 2,77. This corresponds to a ν of 6 (from column 1) and therefore the minimum number of replicate determinations required is $\nu + 1$, or 7. If the user had decided that the acceptable probability of a false acceptance of the same null hypothesis was 0,01 then a minimum of ten replicate determinations (ν of 9) would be required (reading from column 2 ($\beta = 0,01$)).

4.3 CRMs

The user should confirm the suitability of each CRM with respect to the certified value, its uncertainty, method(s) of characterisation, date of certification, statement of intended use, expiry date for unstable CRMs, packaging and storage conditions and special instructions for correct use given in the certificate and the size of test portion required for the measurement process.

4.4 Determinations

The user should perform independent replicate determinations. "Independent", in a practical sense, means that a replicate result is not influenced by previous replicate results. To perform replicate determinations means to repeat the whole procedure.

For example:

a) in the chemical analysis of a solid material, the procedure should be repeated from weighing of the test portion to the final reading or calculating of the result (taking aliquots from the same sample solution is not independent replication);

b) in spectrometric analysis:

   1) the whole process should be repeated for a solid sample, including grinding and surface finishing;

   2) the whole process should be repeated for powder samples from the test portion conditioning.

Independent replicate determinations can be achieved in several ways depending on the nature of the method. In some cases, however, parallel replication is not recommended because an error committed at any step of the procedure could affect all replicates.

The determination results could, if necessary, be scrutinised for possible outliers using the rules described in ISO 5725-2. It should be noted that an excessive number of suspected outliers indicates problems in the analytical method under consideration.