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Guideline for statistical data treatment of inter laboratory tests for validation of analytical methods

Richtlinien für statistische Verfahren der Probenahme und Analyse von Eisen, Stahl und anderen Eisenmetallen

Guide pour le traitement statistique des données de validation de méthodes d'analyse, issues d'essais interlaboratoire

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Guideline for statistical data treatment of inter laboratory tests for validation of analytical methods

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CEN/TR 10345:2008 (E)

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Foreword

This document CEN/TR 10345:2008 has been prepared by Technical Committee ECISS/TC 20 "Methods of chemical analysis of ferrous products", the secretariat of which is held by SIS.

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1 Scope

This document is a guideline to carry out the statistical evaluation of data from an inter laboratory test for method validation.

Its purpose is to detail the methodology of ISO 5725-1, -2 and -3:1994 standards for the treatment of registered data in the conditions used within the ECISS/TC 20 working groups.

NOTE   The present document is not a simplification of ISO 5725 standard, which is the only reference document

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.

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

ISO 5725-2:1994, *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 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

3 Principle

An inter laboratory test for method validation is organised at each stage of the development of a standard draft. Changing economical conditions have lead to the optimisation of the work of the participating laboratories. The principle retained by the ECISS/TC 20 is to have three values by participant laboratory: two values obtained in repeatability conditions (day 1) and a third obtained in intra laboratory reproducibility conditions (day 2). The data evaluation requires a complex statistical analysis, which may be very confusing for a non-specialist, even if it is widely detailed in the ISO 5725:1994 standard. Consequently, it seems useful to clarify the methodology of this standard for the above purpose and to underline that difficulties found should be discussed and solved with statisticians.

Values that are identified as statistically abnormal at 99 % (outliers) using numerical Cochran's and Grubbs' tests lead to the elimination of the laboratory that produced them, at the stage at which they are detected: this principle is adopted even though we risk to wrongly eliminating one result in one hundred. Nevertheless, it is essential to investigate with the laboratory that produced the involved results the reasons for this elimination and to pay particular attention to all of the values produced by this laboratory.

Also, in the case of a laboratory which produces values that are determined as statistically significant at 95 % (stragglers) by numerical Cochran's and Grubbs' tests a particular attention should be paid to all the other values produced by this laboratory.

4 Preliminary rules

4.1 First rule ('to be clear')

The inter laboratory test should be adapted in order to meet the following requirements:

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— to estimate the variances linked to the tested method (repeatability, intra laboratory reproducibility, inter laboratories reproducibility);

— to check that inter laboratories variance is compatible with defined criteria for referee or routine methods (Aim CVR or Max CVR) for their full range of application.

The following must be imposed on the working groups:

a) minimal number of participating laboratories (8 / 10 / 15… - see ISO 5725-1, Annex B);

b) rigorous implementation of the working programme;

c) appropriate number of significant figures to be given for each transmitted value, in order to allow an optimal statistical data evaluation.

4.2 Second rule ('to be modest')

The statistical treatment must be performed by application of the ISO 5725:1994 standard, and by following the here after described procedure. In order to solve the statistical problems encountered, the help of an expert should be sought. It should be noted that the ISO 5725-2 et 5725-3:1994 standards don't give an exhaustive description of all situations and that they clearly indicate that statistical data treatment should be performed by a person experienced in work planning and in statistical analysis (ISO 5725-2 § 6.2). Various situations may arise in practice, which require the application of the variance analysis general modes (ANOVA), these ISO 5725 standards specifying only simplified procedures.

4.3 Minimal characteristics of data population

The number of samples to be tested should be at least two for each range of values to be determined, (for example between 0,010 and 0,099 we must have two samples, between 0,10 and 0,99 we must have two samples and so on), and should never be less than 5 for the full range of values. It is useful, when possible, that the inter laboratory test be performed using CRMs representing at least 50 % of the total number of samples to be tested. The remaining samples can be internal reference materials provided by laboratories on condition that their homogeneity has been tested and found to be compatible with inter laboratory test requirements. These points are not the subject of the present document.

In the present economical situation, an inter laboratory test should be planed with at least 8 laboratories from at least 5 different countries.

The values provided by the participating laboratories should have a sufficient number of significant figures in order to enable correct statistical data treatment; although the number of significant figures does not influence the precision of the result, the transmission of rounded values containing less figures means that the work cannot be correctly evaluated. Expressed as a w/w percentage, values should generally be written under the form listed below, i.e., containing 3 or 4 significant figures:

xx,xx
x,xxx
0,xxxx
0,0xxx
0,00xxx
0,000xxx

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5 Procedure

5.1 Bases

Here we look at the only case where the data population is strictly obtained by the methods defined in § 3, that is to say, 3 determinations for each sample and from each laboratory:

— two determinations in repeatability conditions called 'Day 1,1' et 'Day 1,2';

— supplementary determination in reproducibility conditions called 'Day 2'.

Statistical data evaluation is performed for each content level that is to say in the present case, sample by sample.

5.2 Raw data examination

Raw data must be typed into a table and then printed. The raw data table should be studied in order to detect potential typing errors in the data supplied by each participating laboratory and/or in the final input stage (ISO 5725-2 § 7.2.6).

NOTE   Performing a normality test of the data population to be tested is recommended.

5.3 Intra laboratory repeatability variance (Cochran's test)

A first graphical evaluation of the raw data may be performed in order to test the intra laboratory repeatability consistency by using Mandel's k test (all data included): its only purpose is to get an overview of the data population.

Further statistical treatments are carried out under the hypothesis that the intra laboratory repeatability variances belong to the same normal population. Cochran's test should therefore be performed (ISO 5725-2 § 7.3.3) in order to detect unexpected values of intra laboratory variances, which must then be discarded so that statistical analysis may be pursued.

NOTE 1   Strictly speaking, Cochran's test should only be used to evaluate a population of measurements obtained in repeatability conditions.

In practice, it is advisable to proceed as follows:

— perform Cochran's test with 'Day 1,1' and 'Day 1,2' values, after a normality test for this data population;

— if necessary, discard laboratories having an unexpected variance.

NOTE 2   It is advisable not to perform an iteration when using Cochran's test, except in the case of a large laboratory population (i.e. greater than 15), or when there is a particular statistical reason to justify it. A common rule sometimes used is that the outliers shall not represent more than 10 % of the whole data.

In practice, in order to have a clear view of the data after the Cochran's test has been performed, it is advisable either to print a new table of the remaining data or to clearly identify discarded data.

5.4 Intra laboratory reproducibility variance (Grubbs' test)

Further statistical evaluations are carried out under the hypothesis that intermediate variances (intra laboratory reproducibility) belong to the same normal population. Grubbs' test should be applied (ISO 5725-2 § 7.3.4) in order to detect unexpected means that should then be discarded so that statistical analysis may be pursued.

In practice, it is advisable to proceed in the following order:

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— apply Grubbs' test to the 'daily means' data, that is to say to the pair of values '(Day 1,1 + Day 1,2)/2' and 'Day 2' for all of the laboratories;

— firstly, test the highest 'mean' after having confirmed that the data population is normal;

— if the test is positive, discard the laboratory concerned;

— secondly, test the lowest 'mean';

— if the test is positive, discard the laboratory concerned;

— if neither of the two former tests detect an unexpected 'mean', perform the test with the two highest 'mean' values;

— if the test is positive discard the laboratory(ies) concerned;

— perform the test with the two lowest 'mean' values;

— if the test is positive discard the laboratory(ies) concerned.

NOTE 1   It is advisable not to perform iterations when using Grubbs' test.

NOTE 2   It is not necessary to perform the test whenever the value or the two values to be tested come from a population containing respectively a second or a third identical value.

5.5 Inter laboratory reproducibility variance (Grubbs' test)

A first graphical evaluation of the raw data may be performed in order to test the inter laboratory consistency using Mandel's h test (all retained data remaining after the application of Cochran and Grubbs' tests are included).

Further statistical treatments are carried out under the hypothesis that the laboratories means belong to the same normal population. Grubbs' test should be performed (ISO 5725-2 § 7.3.4) in order to detect unexpected laboratories mean values which must then be discarded so that statistical analysis may be pursued.

In practice, it is advisable to proceed in the following order:

— firstly, test the highest 'laboratory mean', '(Day 1,1 + Day 1,2 + Day 2)/3', after having confirmed that the data population is normal;

— if the test is positive discard the laboratory concerned;

— secondly, test the lowest 'laboratory mean';

— if the test is positive discard the laboratory concerned;

— if neither of the two former tests detect an unexpected 'laboratory mean', perform the test with the two highest 'laboratory mean' values;

— if the test is positive discard the laboratories concerned;

— perform the test with the two lowest 'laboratory mean' values;

— if the test is positive discard the laboratories concerned.

NOTE 1   It is advisable not to perform iterations when using Grubbs' test.

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NOTE 2   It is not necessary to perform the test whenever the value or the two values to be tested come from a population containing respectively a second or a third identical value.

5.6 Retained data examination

The application of Cochran and Grubbs' tests eventually leads to the elimination of raw data from some laboratories. These eliminations have been performed for each content level tested: therefore it is necessary to carry out a critical inter level examination that may lead to discard all data from one or more laboratories if it is established that multiple outlier or straggler values come from these laboratories. These eliminations have to be justified.

In practice, in order to have a clear view of the remaining data, it is advisable either to print a new table of the retained data or to clearly identify discarded data.

5.7 Calculation of the variances associated to the tested method

Calculations are performed with a strict application of the ISO 5725-3 standard (Annex C); it generally results in three variances labelled Vr, VRw and VR.

It is the result of a variance analysis evaluation assessment (ANOVA) which assumes that all the former stages were performed, and which presupposes that intra laboratory repeatability (residual, Vr), intra laboratory reproducibility (VRw) and inter laboratory reproducibility variances (VR) are discernible and quantifiable within the test experiment conditions.

5.8 Treatment for unexpected calculated variances

Despite the implementation of all of the above specifications there could still exist some anomalies:

— variances are normally graded in the order Vr < VRw < VR; if this is not the case it could be that the results of the calculation are not realistic because an hypothesis was not verified; in particular this may occur when the conditions to detect a difference between the intra laboratory reproducibility variance and the residual variance (intra laboratory repeatability variance) don't exist; then strictly speaking, the ISO 5725:1994 standard formulas are not applicable and consequently only one global residual intra laboratory variance can be calculated; the same approach should be taken concerning VRw and VR;

— variances are of course positive numbers (they are the sum of square numbers); nevertheless the ISO 5725:1994 standard formulas can lead to negative values. In such cases these results should not be taken into account because some hypotheses may not have been satisfied or because of the lack in variability of the transmitted data (rounded values or an insufficient number of figures);

— etc...

These anomalies should be dealt with by an expert and the resulting position taken by the committee could be that standard deviation values for repeatability and/or reproducibility don't fit the criteria for publication (ISO 5725-2 § 7.7.2).

5.9 Estimation of a function linking variance and level

Calculations are performed in strict agreement with the specifications of the ISO 5725-2 standard (§ 7.5).

A particular attention should be paid to the correlation coefficient functions between:

— lg m = a + b · lg r

— lg m = a + b · lg Rw

— lg m = a + b · lg R

Typically, the value of each correlation coefficient should be at least greater than 0,9.

Nevertheless, correlation coefficient with values from 0,7 to 0,9 can be admitted, after consensus.

Values lower than 0,7 should be rejected as they show a lack of correlation. In such cases, only individual r, Rw and R should be edited in the validated method (the edition of the smoothed r, Rw and R values is not allowed).

6 Report

The report of the statistical evaluation must be submitted to all of the participating laboratories, so that they can verify that there was no error in the transcription of their results and in order to get their opinion concerning the evaluation performed.

The report of the working group convenor must include:

— complete statistical report;

— participating laboratories corresponding remarks;

— comments and answers of the convenor concerning these remarks.

This report is then sent to the technical committee together with the method accompanied by the remarks and technical comments of the working group members.

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7 General remarks

Most of the inter laboratory tests for the validation of standard methods have not been evaluated under the rules of the present document. Indeed there is no standardised method which mentions the impossibility of the evaluation of one of the three variances, based on the data produced by an inter laboratory test (variances and the corresponding standard deviations calculations are systematically performed and published). It is important to verify if the present document is mentioned in a particular standard for the section concerning the statistical evaluation of the data issued from the corresponding validation inter laboratory test.

It is also hoped to have a software able to perform the statistical evaluation of data produced by an inter laboratory test for method validation, accordingly to the ISO 5725:1994 standard. Nevertheless, it should be kept in mind that there is no software able to make decisions concerning abnormal situations.

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Annex A

Steps for the validation of a Draft Standard

A.1 Decision from a TC to create a working group

Selection of N laboratories: minimum 8 laboratories from not less than 5 countries.

Selection of P samples: minimum 5 and minimum 2 by factor 10 within the measurement range.

Selection of samples: minimum 50 % CRM (if possible).

A.2 Laboratories performance on the specified tests

Rigorous application of the draft standard.

Rigorous application of the previous scheme in order to produce: two results under repeatability conditions "Day 1,1" and "Day 1,2" and one under reproducibility conditions "Day 2".

Transmission of results (%) with the appropriate number of figures: 4 significant figures for values < 1.000 % and 3 significant figures for values > 1.000 %.

A.3 Statistical work to be done at each level (for each of the P samples)

A.3.1 General

General table including all values produced.

Examination of the raw data, for typing errors detection.

Normality test.

A.3.2 Intra laboratory repeatability variance (Cochran's test: ISO 5725-2 § 7.3.3)

Apply only to the set of N couples of values "Day 1,1" and "Day 1,2".

Discard the eventual laboratory(ies) which shows unexpected variance (outliers).

If the outliers represent more than 10 % of the total number of the laboratories, ask for a statistician advice.

Edit a new table containing the set of laboratories having the same "intra laboratory repeatability variance" for further tests.

Normality test.

A.3.3 Intra laboratory reproducibility variance (Grubbs' test: ISO 5725-2 § 7.3.4)

Apply only to the 'daily means': set of 2N values "(A+B)/2" and "C".

Test the highest 'daily mean'.

Discard the eventual laboratory that shows the unexpected variance (outlier).

Test the lowest 'daily mean'.

Discard the eventual laboratory that shows the unexpected variance (outlier).

If neither if the two tests above detect an unexpected 'mean':

Test the couple of highest 'daily mean'.

Discard the eventual laboratory(ies) that show the unexpected variances (outliers).

Test the couple of lowest 'daily mean'.

Discard the eventual laboratory(ies) that show the unexpected variances (outliers).

Edit a new table containing the set of laboratories having the same "intra laboratory reproducibility variance" for further tests.

Normality test.

A.3.4 Inter laboratories reproducibility variance (Grubbs' test: ISO 5725-2 § 7.3.4)

Apply only to the "laboratory means": set of N values "(A+B+C)/3".

Test the highest "mean value".

Discard the eventual laboratory that shows the unexpected variance (outlier).

Test the lowest "mean value".

Discard the eventual laboratory that shows the unexpected variance (outlier).

If neither if the two tests above detect an unexpected 'mean':

Test the couple of highest "mean values".

Discard the eventual laboratories that show the unexpected variances (outliers).

Test the couple of lowest "mean values".

Discard the eventual laboratories that show the unexpected variances (outliers).

Edit a new table containing the set of laboratories having the same inter laboratory reproducibility variance.

A.3.5 Inter level laboratory performance

Discard the whole data from the laboratory(ies) that produced values detected as outliers or stragglers from the 3 tests above at **several** levels.

Consider, if possible, the levels of the h and k Mendel's consistency statistics for the laboratory(ies) to be discarded as a tool to support the decision.

Restart the entire processes of statistical evaluation, without this (or these) laboratory(ies).