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

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

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

Richtlinien für die Behandlung von statistischen Daten von verschiedenen Laboren für die Validierung von Analysenverfahren

This Technical Report was approved by CEN on 29 July 2013. It has been drawn up by the Technical Committee ECISS/TC 102.

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Foreword

This document (CEN/TR 10345:2013) has been prepared by Technical Committee ECISS/TC 102 “Methods of chemical analysis of 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 10345:2008.

In comparison with the previous version of CEN/TR 10345, the following significant technical change was made in Annex A: correction of the error in the last sentence of A.2 concerning the appropriate number of significant figures.

1 Scope

This Technical Report 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 5725-1:1994, ISO 5725-2:1994 and ISO 5725-3:1994 for the treatment of the data collected under the conditions used within the ECISS/TC 102 working groups.

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

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.

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 organized at each stage of the development of a standard draft. Changing economic conditions have led to the optimization of the work of the participating laboratories. The principle retained by ECISS/TC 102 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 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 wrongly eliminating one result in one hundred. Nevertheless, it is essential to advise the laboratory concerned about the reasons for these eliminations and to pay particularly attention to this laboratory's results.

Furthermore, 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, 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:

— 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) within their full range of application.

The following shall be imposed on the working groups:

a) minimal number of participating laboratories (8 / 10 / 15… - see ISO 5725-1:1994, 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 shall be performed by application of the ISO 5725 standard, and by following the procedure described hereafter. In order to solve the statistical problems encountered, the help of an expert should be sought. It should be noted that ISO 5725-2 and ISO 5725-3 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 5725-2:1994, 6.2). Various situations may arise in practice which require the application of the variance analysis general modes (ANOVA), and these ISO 5725 standards only specify simplified procedures.

4.3 Minimal characteristics of data population

At least two samples should be tested for each concentration range to be determined, (for example between 0,010 and 0,099 we shall have two samples, between 0,10 and 0,99 we shall 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 certified reference materials (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.

In the present economic situation, an inter laboratory test should be planned 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 fewer 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,xxx x
0,0xx x
0,00x xx
0,000 xxx

5 Procedure

5.1 Bases

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

— two determinations under repeatability conditions called ‘Day 1,1’ and ‘Day 1,2’;

— the third determination under 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 shall 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 5725-2:1994, 7.2.6).

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 5725-2:1994, 7.3.3) in order to detect unexpected values of intra laboratory variances, which shall then be discarded so that statistical analysis may be pursued.

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;

— discard laboratories having an unexpected variance.

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 5725-2:1994, 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:

— 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 5725-2:1994, 7.3.4) in order to detect unexpected laboratories mean values which shall 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.

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 may lead 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 ISO 5725-3:1994, (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 standard formulae 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 standard formulae 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 significant 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 5725-2:1994, 7.7.2).

5.9 Estimation of a function linking variance and level

Calculations are performed in strict agreement with the specifications of ISO 5725-2:1994, 7.5.

Particular attention should be paid to the correlation coefficient of the functions between:

— $\lg m = a + b \cdot \lg r$

— $\lg m = a + b \cdot \lg Rw$

— 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 shall 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 shall 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.

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 standardized 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 possible to perform the statistical evaluation of the data in accordance with ISO 5725 using software. Nevertheless, it should be kept in mind that there is no software able to make decisions concerning abnormal situations.

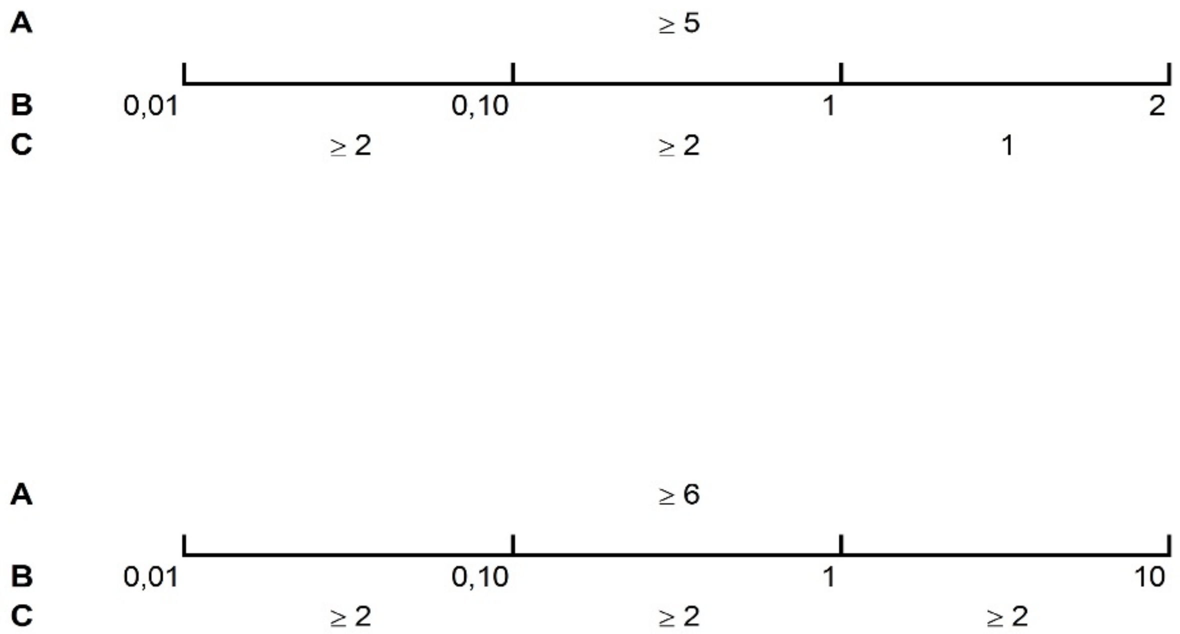
Annex A
(normative)

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: a minimum of 5 samples to cover the entire range. If the range is greater than a factor of 10 then for each sub-range of a factor of 10 there shall be at least 2 samples. See example below:



Key

A minimum number of samples

B content range (in %)

C minimum number of samples for each sub-range of a factor of 10

Figure A.1 — Example of selection of P samples

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: 3 significant figures for values < 0,100 % and 4 significant figures for values ≥ 0,100 %.

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 5725-2:1994, 7.3.3)

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

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

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

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 5725-2:1994, 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 laboratory that shows the unexpected variance (outlier).

Test the lowest 'daily mean'.

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

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

Test the couple of highest 'daily mean'.

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

Test the couple of lowest 'daily mean'.

Discard the 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 5725-2:1994, 7.3.4)

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

Test the highest “mean value”.

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

Test the lowest “mean value”.

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

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

Test the couple of highest “mean values”.

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

Test the couple of lowest “mean values”.

Discard the 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

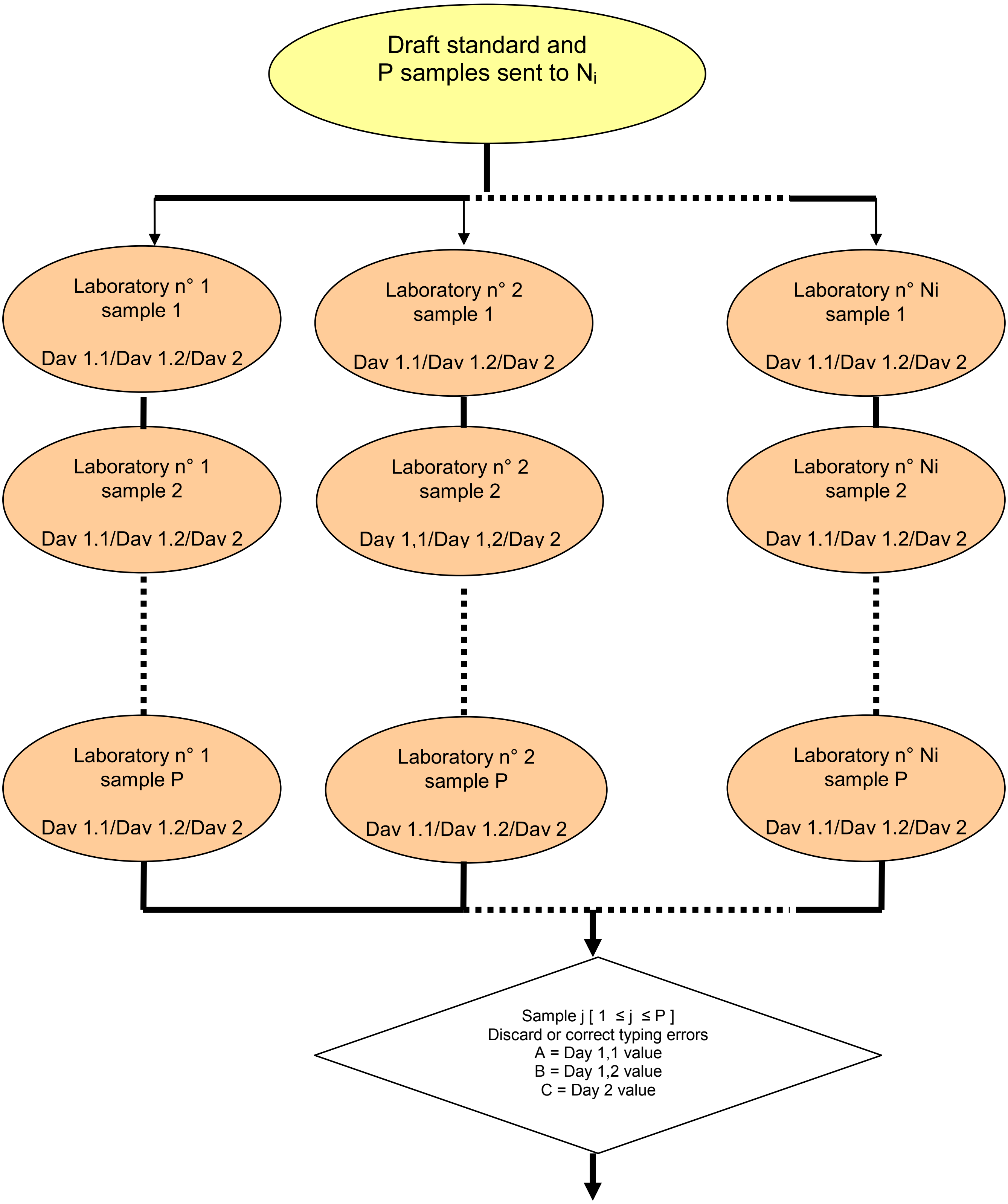
If a laboratory is a straggler or an outlier on several levels the convenor should consider the possibility of rejecting all results from that laboratory.

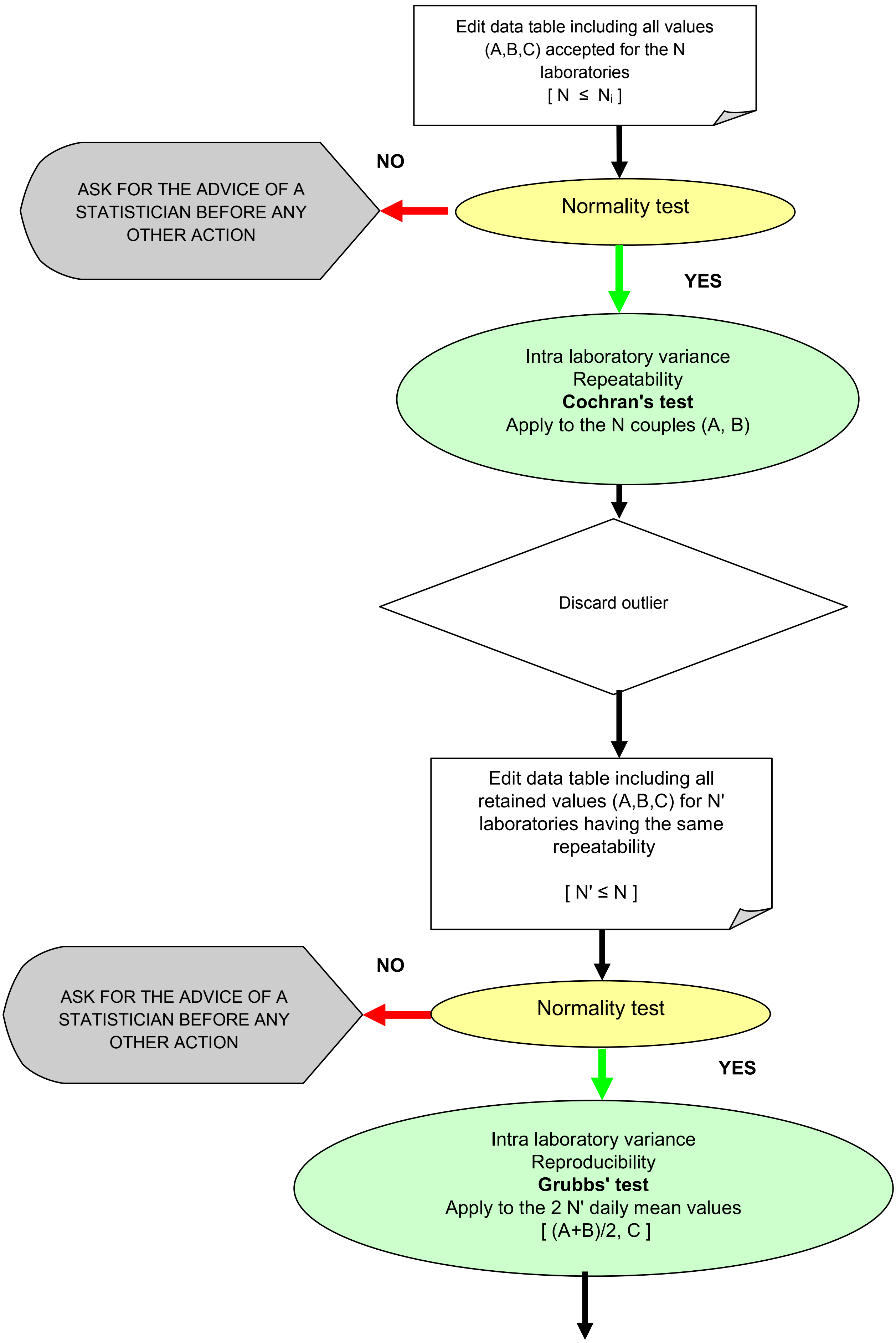
Consider, if possible, the levels of the h and k Mendel's consistency statistics for the laboratory(ies) to be discarded as a tool to support the decision.

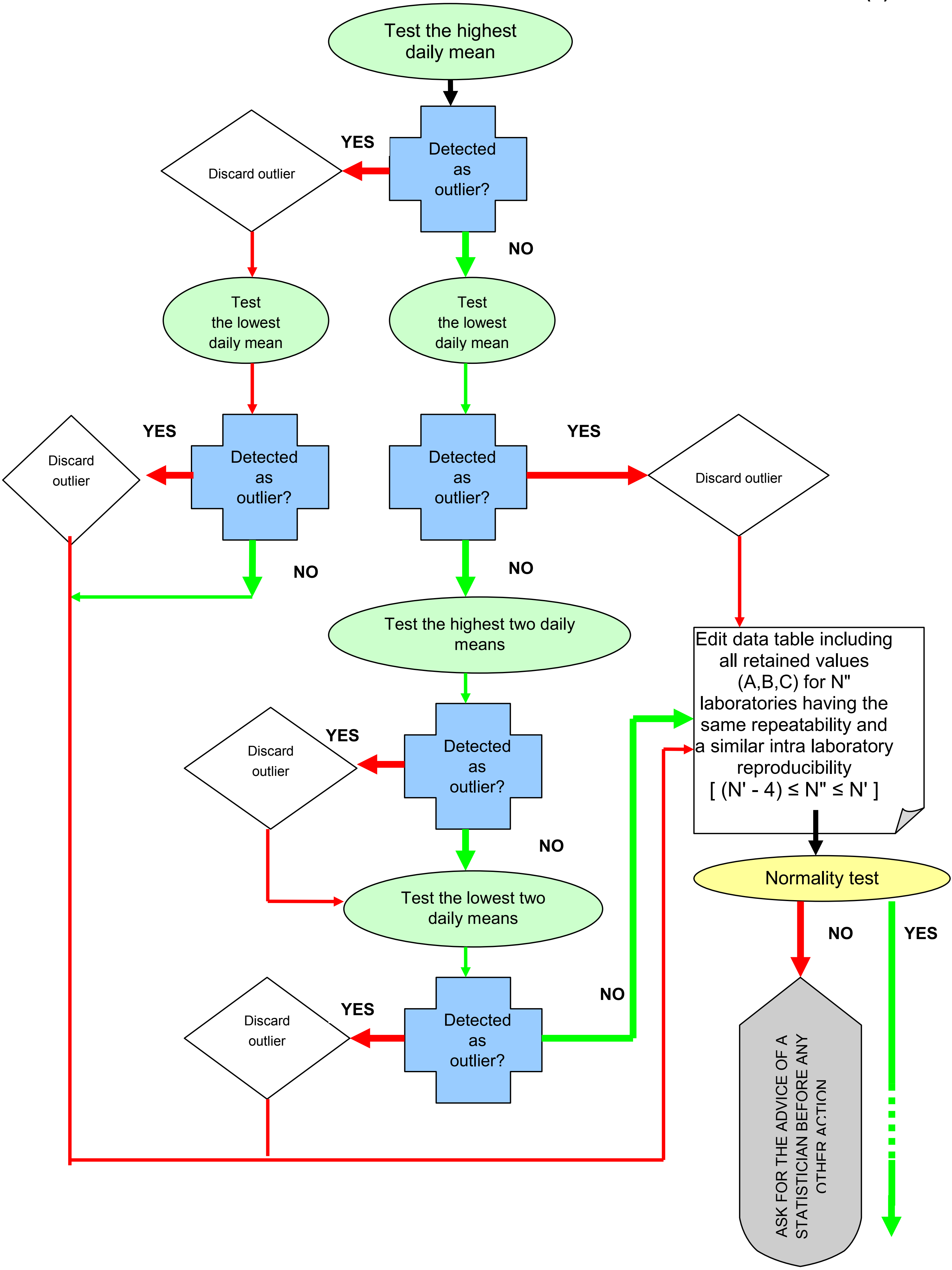
<u>Restart the entire processes of statistical evaluation</u>, without this (or these) laboratory(ies).

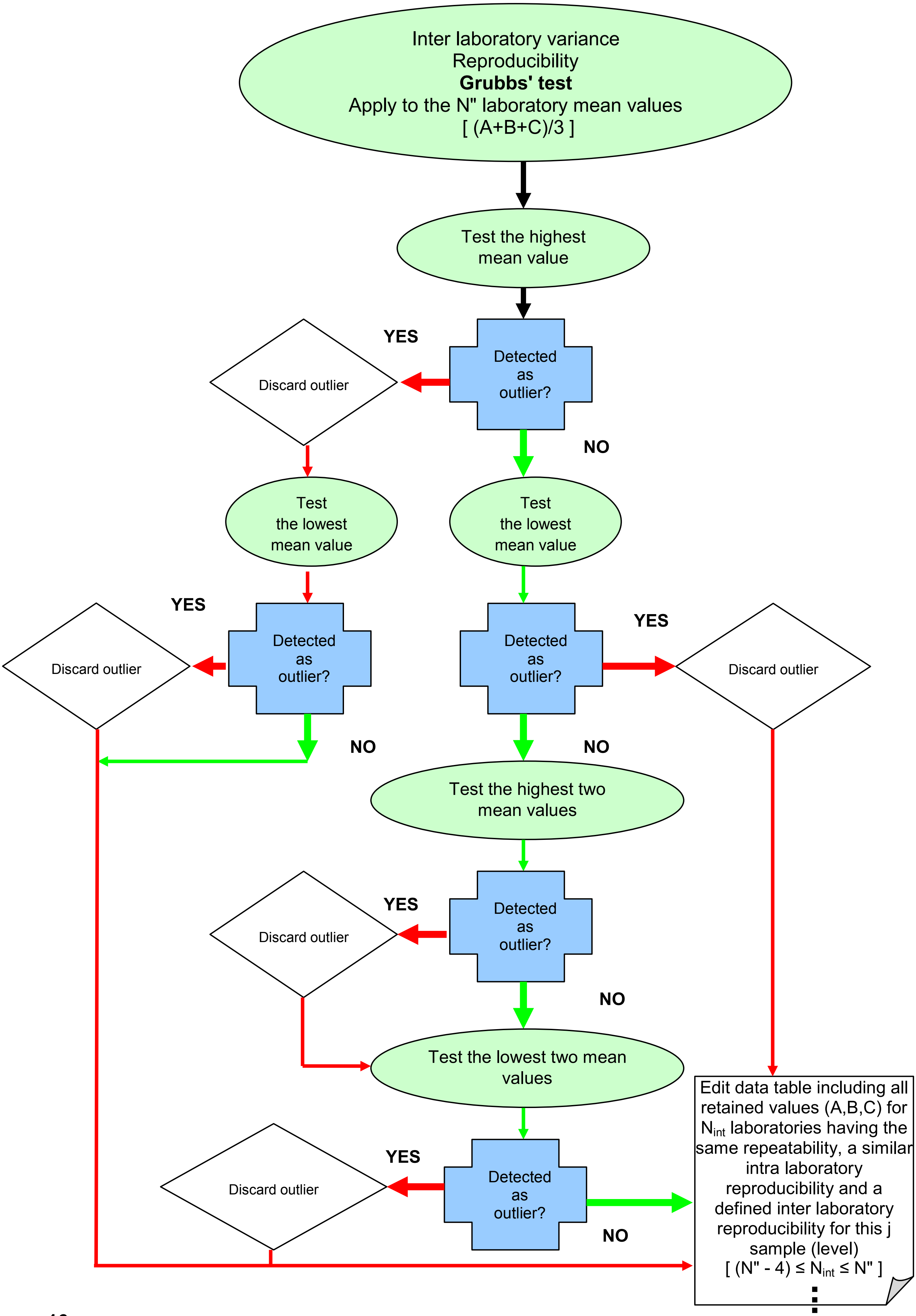
Annex B
(normative)

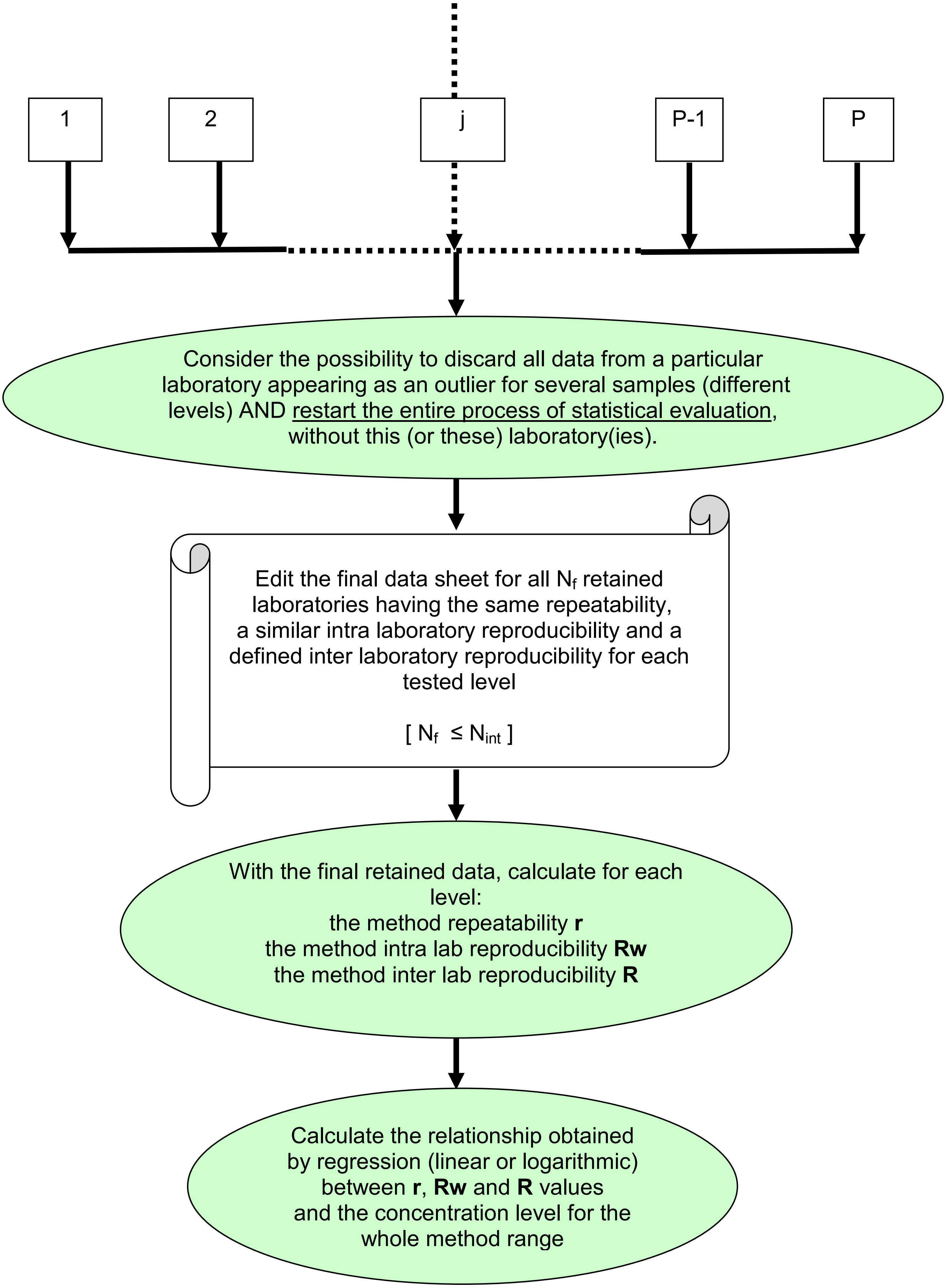
Synoptic of the operations described in Annex A




Edit data table including all values (A,B,C) accepted for the N laboratories
[N ≤ Ni]
Normality test
NO
ASK FOR THE ADVICE OF A STATISTICIAN BEFORE ANY OTHER ACTION
YES
Intra laboratory variance
Repeatability
Cochran's test
Apply to the N couples (A, B)
Discard outlier
Edit data table including all retained values (A,B,C) for N' laboratories having the same repeatability
[N' ≤ N]
Normality test
NO
ASK FOR THE ADVICE OF A STATISTICIAN BEFORE ANY OTHER ACTION
YES
Intra laboratory variance
Reproducibility
Grubbs' test
Apply to the 2 N' daily mean values
[(A+B)/2, C]


Test the highest daily mean
Detected as outlier?
YES
Discard outlier
NO
Test the lowest daily mean
Test the lowest daily mean
Detected as outlier?
YES
Discard outlier
NO
Detected as outlier?
YES
Discard outlier
NO
Test the highest two daily means
Edit data table including all retained values (A,B,C) for N" laboratories having the same repeatability and a similar intra laboratory reproducibility [(N' - 4) ≤ N" ≤ N']
Detected as outlier?
YES
Discard outlier
NO
Normality test
Test the lowest two daily means
NO
YES
Detected as outlier?
YES
Discard outlier
NO
ASK FOR THE ADVICE OF A STATISTICIAN BEFORE ANY OTHER ACTION


Inter laboratory variance
Reproducibility
Grubbs' test
Apply to the N" laboratory mean values
[(A+B+C)/3]
Test the highest mean value
Detected as outlier?
YES
Discard outlier
NO
Test the lowest mean value
Test the lowest mean value
Detected as outlier?
YES
Discard outlier
NO
Detected as outlier?
YES
Discard outlier
NO
Test the highest two mean values
Detected as outlier?
YES
Discard outlier
NO
Test the lowest two mean values
Detected as outlier?
YES
Discard outlier
NO
Edit data table including all retained values (A,B,C) for N_int laboratories having the same repeatability, a similar intra laboratory reproducibility and a defined inter laboratory reproducibility for this j sample (level)
[(N" - 4) ≤ N_int ≤ N"]


1
2
j
P-1
P
Consider the possibility to discard all data from a particular laboratory appearing as an outlier for several samples (different levels) AND restart the entire process of statistical evaluation, without this (or these) laboratory(ies).
Edit the final data sheet for all N_f retained laboratories having the same repeatability, a similar intra laboratory reproducibility and a defined inter laboratory reproducibility for each tested level
[$N_f \leq N_{int}$]
With the final retained data, calculate for each level:
the method repeatability **r**
the method intra lab reproducibility **Rw**
the method inter lab reproducibility **R**
Calculate the relationship obtained by regression (linear or logarithmic) between **r**, **Rw** and **R** values and the concentration level for the whole method range

Annex C
(informative)

Examples

C.1 Nickel alloys – Determination of tantalum content – Inductively coupled plasma emission spectrometric method – ISO 22725

Sample 8-2-Ta

C.1.1 Original data

Laboratory	Day 1	Day 2
LAB 1	0,137 5	0,139 1
	0,138 2	
LAB 2	0,139 6	0,134 5
	0,135 8	
LAB 3	0,145 0	0,147 0
	0,147 0	
LAB 4	0,133 8	0,131 8
	0,133 5	
LAB 5	0,148 5	0,149 7
	0,151 0	
LAB 6	0,143 1	0,139 6
	0,140 4	
LAB 7	0,136 6	0,134 2
	0,148 3	
LAB 8	0,126 0	0,127 0
	0,126 0	
LAB 9	0,137 9	0,140 1
	0,139 1	

NOTE The “Day 1” mean values (to be submitted to the Cochran test) have a normal distribution [test of Shapiro and Wilk and test of Kolmogorov-Smirnov].

C.1.2 Cochran test

Only values produced in "Day 1" are tested:

Laboratory	Ta values (%)	Standard deviation	Variance
LAB 1	0,137 5	0,000 495	0,000 000 245
	0,138 2		
LAB 2	0,139 6	0,002 687	0,000 007 220
	0,135 8		
LAB 3	0,145 0	0,001 414 2	0,000 002 000
	0,147 0		
LAB 4	0,133 8	0,000 212 1	0,000 000 045
	0,133 5		
LAB 5	0,148 5	0,001 767 8	0,000 003 125
	0,151 0		
LAB 6	0,143 1	0,001 909 2	0,000 003 645
	0,140 4		
LAB 7	0,136 6	0,008 273 1	0,000 068 445
	0,148 3		
LAB 8	0,126 0	0	0
	0,126 0		
LAB 9	0,137 9	0,000 848 5	0,000 000 720
	0,139 1		
		Variance sum	0,000 085 4
		Maximum variance	0,000 068 4
		Cochran ratio	0,801
		Critical value [p = 9; n = 2; 99 %]	0,754
		Critical value [p = 9; n = 2; 95 %]	0,638

The highest variance (corresponding to "LAB 7" values) is a Cochran outlier. Values from this laboratory are removed before proceeding to the next test.

C.1.3 New table containing the set of laboratories having the same intra laboratory repeatability variance for further tests

The data from the laboratories having the same intra laboratory repeatability variance are edited in a new table:

Laboratory	Day 1	Day 2
LAB 1	0,137 5	0,139 1
	0,138 2	
LAB 2	0,139 6	0,134 5
	0,135 8	
LAB 3	0,145 0	0,147 0
	0,147 0	
LAB 4	0,133 8	0,131 8
	0,133 5	
LAB 5	0,148 5	0,149 7
	0,151 0	
LAB 6	0,143 1	0,139 6
	0,140 4	
LAB 8	0,126 0	0,127 0
	0,126 0	
LAB 9	0,137 9	0,140 1
	0,139 1	

NOTE The "Day 1" mean values and the values of "Day 2" (to be submitted to the intra laboratory reproducibility variance Grubbs test) have a normal distribution [test of Shapiro and Wilk and test of Kolmogorov-Smirnov].

C.1.4 Grubbs test, for intra laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "mean value of Day 1" and to the "value of Day 2".

In this case, 2 × 8 values are tested:

Day	Laboratory	Ta values (%)
Mean values from Day 1	LAB 1	0,137 9
	LAB 2	0,137 7
	LAB 3	0,146 0
	LAB 4	0,133 7
	LAB 5	0,149 8
	LAB 6	0,141 8
	LAB 8	0,126 0
	LAB 9	0,138 5
Values from Day 2	LAB 1	0,139 1
	LAB 2	0,134 5
	LAB 3	0,147 0
	LAB 4	0,131 8
	LAB 5	0,149 7
	LAB 6	0,139 6
	LAB 8	0,127 0
	LAB 9	0,140 1
	Mean value	0,138 8
	Standard deviation	0,007 2
	Maximum value	0,149 8
	Minimum value	0,126 0
	Grubbs result for the maximum value	1,537
	Grubbs result for the minimum value	1,782
	Critical value [*p* = 16; 99 %] Critical value [*p* = 16; 95 %]	2,852 2,585

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test “by pairs” is then performed:

Day	Laboratory	Ta values (%)	Test for the 2 lowest values	Test for the 2 highest values
Mean values from Day 1	LAB 1	0,137 9		0,126 0
	LAB 2	0,137 7		0,127 0
	LAB 3	0,146 0	0,131 8	0,131 8
	LAB 4	0,133 7	0,133 7	0,133 7
	LAB 5	0,149 8	0,134 5	0,134 5
	LAB 6	0,141 8	0,137 7	0,137 7
	LAB 8	0,126 0	0,137 9	0,137 9
	LAB 9	0,138 5	0,138 5	0,138 5
Values from Day 2	LAB 1	0,139 1	0,139 1	0,139 1
	LAB 2	0,134 5	0,139 6	0,139 6
	LAB 3	0,147 0	0,140 1	0,140 1
	LAB 4	0,131 8	0,141 8	0,141 8
	LAB 5	0,149 7	0,146 0	0,146 0
	LAB 6	0,139 6	0,147 0	0,147 0
	LAB 8	0,127 0	0,149 7	
	LAB 9	0,140 1	0,149 8	
	Mean value	0,138 8	0,140 5	0,137 2
	Standard deviation	0,007 2	0,005 7	0,006 2
	Variance	0,000 051	0,000 033	0,000 038
	Grubbs result for the lowest pair		0,552 8	
	Grubbs result for the highest pair			0,641 6
	Critical value [p = 16; 99 %] Critical value [p = 16; 95 %]	0,276 7 0,360 3		

C.1.5 New table containing the set of laboratories having the same intra laboratory reproducibility variance for further tests

No outliers were found in C.1.4. The table from C.1.3 is still valid.

NOTE The “overall mean values of each set of data” (to be submitted to the inter laboratory reproducibility variance Grubbs test) have a normal distribution [test of Shapiro and Wilk and test of Kolmogorov-Smirnov].

C.1.6 Grubbs test, for inter laboratory reproducibility variance

The one-sided Grubbs’ test is performed on the data corresponding to the “overall mean value of each set of data”.

In this case, eight values are tested:

Laboratory	Ta mean values (%)
LAB 1	0,138 3
LAB 2	0,136 6
LAB 3	0,146 3
LAB 4	0,133 0
LAB 5	0,149 7
LAB 6	0,141 0
LAB 8	0,126 3
LAB 9	0,139 0
Mean value	0,138 8
Standard deviation	0,007 3
Maximum value	0,149 7
Minimum value	0,126 3
Grubbs result for the maximum value	1,494
Grubbs result for the minimum value	1,703
Critical value [*p* = 8; 99 %] Critical value [*p* = 8; 95 %]	2,274 2,126

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test “by pairs” is then performed:

Laboratory	Ta mean values (%)	Test for the 2 lowest values	Test for the 2 highest values
LAB 1	0,138 3		0,126 3
LAB 2	0,136 6		0,133 0
LAB 3	0,146 3	0,136 6	0,136 6
LAB 4	0,133 0	0,138 3	0,138 3
LAB 5	0,149 7	0,139 0	0,139 0
LAB 6	0,141 0	0,141 0	0,141 0
LAB 8	0,126 3	0,146 3	
LAB 9	0,139 0	0,149 7	
Mean value	0,138 8	0,141 8	0,135 7
Standard deviation	0,007 3	0,005 1	0,005 3
Variance	0,000 054	0,000 026	0,000 028
Grubbs result for the lowest pair		0,349 1	
Grubbs result for the highest pair			0,378 3
Critical value [*p* = 8; 99 %] Critical value [*p* = 8; 95 %]	0,056 3 0,110 1		

C.1.7 New table containing the set of laboratories having the same inter laboratory reproducibility variance for further evaluations

No outliers were found in C.1.6. The table from C.1.3 is still valid and includes all the retained values.

C.2 Steel and iron – Determination of Nitrogen content –Thermal conductimetric method after fusion in a current of inert gas – ISO 10720

Sample 27-6

C.2.1 Original data

Laboratory	Day 1	Day 2
LAB 1	0,021 8	0,021 9
	0,021 8	
LAB 2	0,022 4	0,022 0
	0,022 2	
LAB 3	0,021 7	0,021 4
	0,021 7	
LAB 4	0,030 9	0,032 3
	0,032 2	
LAB 5	0,023 0	0,021 0
	0,023 0	
LAB 6	0,022 8	0,023 0
	0,022 9	
LAB 7	0,022 9	0,022 6
	0,022 0	
LAB 8	0,022 9	0,021 5
	0,021 1	
LAB 9	0,022 5	0,022 3
	0,022 7	
LAB 10	0,023 1	0,022 4
	0,022 7	
LAB 11	0,020 4	0,021 4
	0,019 4	
LAB 12	0,019 5	0,020 5
	0,020 1	
LAB 13	0,018 6	0,019 1
	0,015 9	
LAB 14	0,023 7	0,023 4
	0,023 7	

NOTE The "Day 1" mean values (to be submitted to the Cochran test) do not have a normal distribution at 95 % and 99 % confidence levels [test of Shapiro and Wilk] and at 95 % confidence level [test of Kolmogorov-Smirnov].

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.2.2 Cochran test

Only values produced in “Day 1” are tested:

Laboratory	N values (%)	Standard deviation	Variance
LAB 1	0,021 8 0,021 8	0	0
LAB 2	0,022 4 0,022 2	0,000 141 421	0,000 000 020
LAB 3	0,021 7 0,021 7	0	0
LAB 4	0,030 9 0,032 2	0,000 919 239	0,000 000 845
LAB 5	0,023 0 0,023 0	0	0
LAB 6	0,022 8 0,022 9	0,000 070 711	0,000 000 005
LAB 7	0,022 9 0,022 0	0,000 636 396	0,000 000 405
LAB 8	0,022 9 0,021 1	0,001 272 792	0,000 001 620
LAB 9	0,022 5 0,022 7	0,000 141 421	0,000 000 020
LAB 10	0,023 1 0,022 7	0,000 282 843	0,000 000 080
LAB 11	0,020 4 0,019 4	0,000 707 107	0,000 000 500
LAB 12	0,019 5 0,020 1	0,000 424 264	0,000 000 180
LAB 13	0,018 6 0,015 9	0,001 909 188	0,000 003 645
LAB 14	0,023 7 0,023 7	0	0
		Variance sum	0,000 007 320
		Maximum variance	0,000 003 645
		Cochran ratio	0,498
		Critical value [p = 14; n = 2; 99 %] Critical value [p = 14; n = 2; 95 %]	0,599 0,492

Values from “LAB 13” appear as stragglers, but no outliers are found.

C.2.3 New table containing the set of laboratories having the same intra laboratory repeatability variance for further tests

No outliers were found in C.2.2. The table from C.2.1 is still valid.

NOTE The “Day 1” mean values and the values of “Day 2” (to be submitted to the intra laboratory reproducibility variance Grubbs test) do not have a normal distribution [tests of Shapiro and Wilk and of Kolmogorov-Smirnov at 99 % confidence level].

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.2.4 Grubbs test, for intra laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "mean value of Day 1" and to the "value of Day 2". In this case, 2 × 14 values are tested:

Day	Laboratory	N mean values (%)
Mean values from Day 1	LAB 1	0,021 8
	LAB 2	0,022 3
	LAB 3	0,021 7
	LAB 4	0,031 6
	LAB 5	0,023 0
	LAB 6	0,022 9
	LAB 7	0,022 5
	LAB 8	0,022 0
	LAB 9	0,022 6
	LAB 10	0,022 9
	LAB 11	0,019 9
	LAB 12	0,019 8
	LAB 13	0,017 3
	LAB 14	0,023 7
Values from Day 2	LAB 1	0,021 9
	LAB 2	0,022 0
	LAB 3	0,021 4
	LAB 4	0,032 3
	LAB 5	0,021 0
	LAB 6	0,023 0
	LAB 7	0,022 6
	LAB 8	0,021 5
	LAB 9	0,022 3
	LAB 10	0,022 4
	LAB 11	0,021 4
	LAB 12	0,020 5
	LAB 13	0,019 1
	LAB 14	0,023 4
	Mean value	0,022 5
	Standard deviation	0,003 0
	Maximum value	0,032 3
	Minimum value	0,017 3
	Grubbs result for the maximum value	3,264
	Grubbs result for the minimum value	1,723
	Critical value [p = 28; 99 %] Critical value [p = 28; 95 %]	3,199 2,876

The value 0,032 3 %, produced by “LAB 4” in Day 2, is an outlier.

Consequently, both values obtained by “LAB 4” for this sample are removed before performing the one-sided Grubbs test to the lowest “daily mean”.

The test is performed on 2 × 13 values:

Day	Laboratory	N mean values (%)
Mean values from Day 1	LAB 1	0,021 8
	LAB 2	0,022 3
	LAB 3	0,021 7
	LAB 5	0,023 0
	LAB 6	0,022 9
	LAB 7	0,022 5
	LAB 8	0,022 0
	LAB 9	0,022 6
	LAB 10	0,022 9
	LAB 11	0,019 9
	LAB 12	0,019 8
	LAB 13	0,017 3
	LAB 14	0,023 7
Values from Day 2	LAB 1	0,021 9
	LAB 2	0,022 0
	LAB 3	0,021 4
	LAB 5	0,021 0
	LAB 6	0,023 0
	LAB 7	0,022 6
	LAB 8	0,021 5
	LAB 9	0,022 3
	LAB 10	0,022 4
	LAB 11	0,021 4
	LAB 12	0,020 5
	LAB 13	0,019 1
	LAB 14	0,023 4
	Mean value	0,021 7
	Standard deviation	0,001 4
	Maximum value	0,023 7
	Minimum value	0,017 3
	Grubbs result for the maximum value	1,369
	Grubbs result for the minimum value	3,094
	Critical value [*p* = 26; 99 %] Critical value [*p* = 26; 95 %]	3,157 2,841

The Day 1 mean value from “LAB 13” appears as a straggler (0,017 3 %), but no outlier was found.

The Grubbs test “by pairs” is NOT performed in this case, as an outlier was found after application of the one-sided test.

C.2.5 New table containing the set of laboratories having the same intra laboratory reproducibility variance for further tests

The data from the laboratories having the same intra laboratory reproducibility variance are edited in a new table:

Laboratory	Day 1	Day 2
LAB 1	0,021 8	0,021 9
	0,021 8	
LAB 2	0,022 4	0,022 0
	0,022 2	
LAB 3	0,021 7	0,021 4
	0,021 7	
LAB 5	0,023 0	0,021 0
	0,023 0	
LAB 6	0,022 8	0,023 0
	0,022 9	
LAB 7	0,022 9	0,022 6
	0,022 0	
LAB 8	0,022 9	0,021 5
	0,021 1	
LAB 9	0,022 5	0,022 3
	0,022 7	
LAB 10	0,023 1	0,022 4
	0,022 7	
LAB 11	0,020 4	0,021 4
	0,019 4	
LAB 12	0,019 5	0,020 5
	0,020 1	
LAB 13	0,018 6	0,019 1
	0,015 9	
LAB 14	0,023 7	0,023 4
	0,023 7	

NOTE The “overall mean values of each set of data” (to be submitted to the inter laboratory reproducibility variance Grubbs test) have a normal distribution [tests of Shapiro and Wilk and of Kolmogorov-Smirnov at 99 % confidence level].

At the 95 % confidence level, this distribution doesn’t follow the normal law [after application of both tests].

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.2.6 Grubbs test, for inter laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "overall mean value of each set of remaining data".

In this case, 13 values are tested:

Laboratory	**N mean values (%)**
LAB 1	0,021 8
LAB 2	0,022 2
LAB 3	0,021 6
LAB 5	0,022 3
LAB 6	0,022 9
LAB 7	0,022 5
LAB 8	0,021 8
LAB 9	0,022 5
LAB 10	0,022 7
LAB 11	0,020 4
LAB 12	0,020 0
LAB 13	0,017 9
LAB 14	0,023 6
Mean value	0,021 7
Standard deviation	0,001 5
Maximum value	0,023 6
Minimum value	0,017 9
Grubbs result for the maximum value	1,249
Grubbs result for the minimum value	2,556
Critical value [*p* = 13; 99 %] Critical value [*p* = 13; 95 %]	2,699 2,462

The mean value from "LAB 13" appears as a straggler (0,017 9 %), but no outliers are found.

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test “by pairs” is then performed:

Laboratory	N mean values (%)	Test for the 2 lowest values	Test for the 2 highest values
LAB 1	0,021 8		0,017 9
LAB 2	0,022 2		0,020 0
LAB 3	0,021 6	0,020 4	0,020 4
LAB 5	0,022 3	0,021 6	0,021 6
LAB 6	0,022 9	0,021 8	0,021 8
LAB 7	0,022 5	0,021 8	0,021 8
LAB 8	0,021 8	0,022 2	0,022 2
LAB 9	0,022 5	0,022 3	0,022 3
LAB 10	0,022 7	0,022 5	0,022 5
LAB 11	0,020 4	0,022 5	0,022 5
LAB 12	0,020 0	0,022 7	0,022 7
LAB 13	0,017 9	0,022 9	
LAB 14	0,023 6	0,023 6	
Mean value	0,021 7	0,022 2	0,021 4
Standard deviation	0,001 5	0,000 8	0,001 5
Variance	0,000 002 27	0,000 000 68	0,000 002 15
Grubbs result for the lowest pair		0,249 4	
Grubbs result for the highest pair			0,787 4
Critical value [*p* = 13; 99 %] Critical value [*p* = 13; 95 %]	0,201 6 0,283 6		

The overall mean values 0,017 9 and 0,020 0 % (produced by LAB 13 and LAB 12, respectively) are stranglers, but NOT outliers.

C.2.7 New table containing the set of laboratories having the same inter laboratory reproducibility variance for further evaluations

No outliers were found in C.2.6. The table from C.2.5 is still valid and includes all the retained values.

C.3 Steel and iron – Determination of chromium content – Indirect titration method – ISO 15355

Sample 43-3

C.3.1 Original data

Laboratory	Day 1	Day 2
LAB 1	3,986	3,980
	3,982	
LAB 2	3,996	3,981
	3,987	
LAB 3	4,040	4,070
	4,040	
LAB 4	3,955	3,962
	3,964	
LAB 5	3,953	3,965
	3,961	
LAB 6	3,991	3,982
	3,979	

NOTE The “Day 1” mean values (to be submitted to the Cochran test) have a normal distribution [test of Shapiro and Wilk and test of Kolmogorov-Smirnov].

C.3.2 Cochran test

Only values produced in “Day 1” are tested:

Laboratory	Cr values (%)	Standard deviation	Variance
LAB 1	3,986	0,002 828 4	0,000 008 0
	3,982		
LAB 2	3,996	0,006 364	0,000 040 5
	3,987		
LAB 3	4,040	0	0
	4,040		
LAB 4	3,955	0,006 364	0,000 040 5
	3,964		
LAB 5	3,953	0,005 656 9	0,000 032 0
	3,961		
LAB 6	3;991	0,008 485 3	0,000 072 0
	3,979		
		Variance sum	0,000 193
		Maximum variance	0,000 072
		Cochran ratio	0,373
		Critical value [p = 6; n = 2; 99 %] Critical value [p = 6; n = 2; 95 %]	0,883 0,781

No laboratory shows unexpected intra laboratory repeatability variance (no outliers, no stragglers).

C.3.3 New table containing the set of laboratories having the same intra laboratory repeatability variance for further tests

No outliers were found in C.2.2. The table from C.2.1 is still valid.

NOTE The "Day 1" mean values and the values of "Day 2" (to be submitted to the intra laboratory reproducibility variance Grubbs test) do not have a normal distribution [tests of Shapiro and Wilk and of Kolmogorov-Smirnov at 99 % confidence level].

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.3.4 Grubbs test, for intra laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "mean value of Day 1" and to the "value of Day 2".

In this case, 2 × 6 values are tested:

Day	Laboratory	Cr values (%)
Mean values from Day 1	LAB 1	3,984 0
	LAB 2	3,991 5
	LAB 3	4,040 0
	LAB 4	3,959 5
	LAB 5	3,957 0
	LAB 6	3,985 0
Values from Day 2	LAB 1	3,980 0
	LAB 2	3,981 0
	LAB 3	4,070 0
	LAB 4	3,962 0
	LAB 5	3,965 0
	LAB 6	3,982 0
	Mean value	3,988 1
	Standard deviation	0,033 8
	Maximum value	4,070 0
	Minimum value	3,957 0
	Grubbs result for the maximum value	2,421
	Grubbs result for the minimum value	0,919
	Critical value [*p* = 12; 99 %] Critical value [*p* = 12; 95 %]	2,636 2,412

The value 4,070 0 %, produced by "LAB 3" is a straggler, but NOT an outlier.

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test "by pairs" is then performed:

Day	Laboratory	Cr values (%)	Test for the 2 lowest values	Test for the 2 highest values
Mean values from Day 1	LAB 1	3,984 0		3,957 0
	LAB 2	3,991 5		3,959 5
	LAB 3	4,040 0	3,962 0	3,962 0
	LAB 4	3,959 5	3,965 0	3,965 0
	LAB 5	3,957 0	3,980 0	3,980 0
	LAB 6	3,985 0	3,981 0	3,981 0
Values from Day 2	LAB 1	3,980 0	3,982 0	3,982 0
	LAB 2	3,981 0	3,984 0	3,984 0
	LAB 3	4,070 0	3,985 0	3,985 0
	LAB 4	3,962 0	3,991 5	3,991 5
	LAB 5	3,965 0	4,040 0	
	LAB 6	3,982 0	4,070 0	
	Mean value	3,988 1	3,994 1	3,974 7
	Standard deviation	0,033 8	0,034 1	0,012 5
	Variance	0,001 144 765	0,001 161 469	0,000 155 067
	Grubbs result for the lowest pair		0,830 1	
	Grubbs result for the highest pair			0,110 8
	Critical value [*p* = 12; 99 %] Critical value [*p* = 12; 95 %]	0,173 8 0,253 7		

The highest pair (corresponding to "LAB 3" values) is a Grubbs outlier. These values are removed before proceeding to the next test.

C.3.5 New table containing the set of laboratories having the same intra laboratory reproducibility variance for further tests

The data from the laboratories having the same intra laboratory reproducibility variance are edited in a new table:

Laboratory	Day 1	Day 2
LAB 1	3,986	3,980
	3,982	
LAB 2	3,996	3,981
	3,987	
LAB 4	3,955	3,962
	3,964	
LAB 5	3,953	3,965
	3,961	
LAB 6	3,991	3,982
	3,979	

NOTE The "overall mean values of each set of data" (to be submitted to the inter laboratory reproducibility variance Grubbs test) have a normal distribution [test of Shapiro and Wilk and test of Kolmogorov-Smirnov].

C.3.6 Grubbs test, for inter laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "overall mean value of each set of remaining data".

In this case, five values are tested:

Laboratory	Cr mean values (%)
LAB 1	3,982 7
LAB 2	3,988 0
LAB 4	3,960 3
LAB 5	3,959 7
LAB 6	3,984 0
Mean value	3,974 9
Standard deviation	0,013 8
Maximum value	3,988 0
Minimum value	3,959 7
Grubbs result for the maximum value	0,946
Grubbs result for the minimum value	1,108
Critical value [p = 5; 99 %] Critical value [p = 5; 95 %]	1,764 1,715

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test “by pairs” is then performed:

Laboratory	Cr mean values (%)	Test for the 2 lowest values	Test for the 2 highest values
LAB 1	3,982 7		3,959 7
LAB 2	3,988 0		3,960 3
LAB 4	3,960 3	3,982 7	3,982 7
LAB 5	3,959 7	3,984 0	
LAB 6	3,984 0	3,988 0	
Mean value	3,974 9	3,984 9	3,967 6
Standard deviation	0,013 8	0,002 8	0,013 1
Variance	0,000 189 744	0,000 007 704	0,000 171 370
Grubbs result for the lowest pair		0,020 3	
Grubbs result for the highest pair			0,451 6
Critical value [*p* = 5; 99 %] Critical value [*p* = 5; 95 %]	0,001 8 0,009 0		

C.3.7 New table containing the set of laboratories having the same inter laboratory reproducibility variance for further evaluations

No outliers were found in C.2.6. The table from C.2.5 is still valid and includes all the retained values.

C.4 Steel and iron – Determination of Nitrogen content –Thermal conductimetric method after fusion in a current of inert gas – ISO 10720

Sample 27-1

C.4.1 Original data

Laboratory	Day 1	Day 2
LAB 1	0,000 7	0,000 8
	0,000 7	
LAB 2	0,001 3	0,001 4
	0,001 1	
LAB 3	0,000 7	0,000 7
	0,000 8	
LAB 4	0,000 5	0,001 6
	0,000 6	
LAB 5	0,000 5	0,000 7
	0,000 8	
LAB 6	0,001 0	0,000 7
	0,001 0	
LAB 7	0,000 5	0,000 4
	0,000 5	
LAB 8	0,000 9	0,000 9
	0,000 8	
LAB 9	0,000 9	0,000 8
	0,000 8	
LAB 10	0,000 9	0,000 9
	0,000 8	
LAB 11	0,000 7	0,000 7
	0,000 7	
LAB 12	0,001 0	0,000 7
	0,000 9	
LAB 13	0,001 5	0,001 3
	0,0018	
LAB 14	0,000 7	0,000 7
	0,000 8	

NOTE The "Day 1" mean values (to be submitted to the Cochran test) have a normal distribution, excepted considering the 95 % confidence level from the test of Shapiro and Wilk.

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.4.2 Cochran test

Only values produced in “Day 1” are tested:

Laboratory	N values (%)	Standard deviation	Variance
LAB 1	0,000 7 0,000 7	0	0
LAB 2	0,001 3 0,001 1	0,000 141	0,000 000 020 0
LAB 3	0,000 7 0,000 8	0,000 071	0,000 000 005 0
LAB 4	0,000 5 0,000 6	0,000 071	0,000 000 005 0
LAB 5	0,000 5 0,000 8	0,000 212	0,000 000 045 0
LAB 6	0,001 0 0,001 0	0	0
LAB 7	0,000 5 0,000 5	0	0
LAB 8	0,000 9 0,000 8	0,000 071	0,000 000 005 0
LAB 9	0,000 9 0,000 8	0,000 071	0,000 000 005 0
LAB 10	0,000 9 0,000 8	0,000 071	0,000 000 005 0
LAB 11	0,000 7 0,000 7	0	0
LAB 12	0,001 0 0,000 9	0,000 071	0,000 000 005 0
LAB 13	0,001 5 0,001 8	0,000 212	0,000 000 045 0
LAB 14	0,000 7 0,000 8	0,000 071	0,000 000 005 0
		Variance sum	0,000 000 145
		Maximum variance	0,000 000 045
		Cochran ratio	0,310
		Critical value [p = 14; n = 2; 99 %] Critical value [p = 14; n = 2; 95 %]	0,599 0,492

No laboratory shows unexpected intra laboratory repeatability variance (no outliers, no stragglers).

C.4.3 New table containing the set of laboratories having the same intra laboratory repeatability variance for further tests

No outliers were found in C.4.2. The table from C.4.1 is still valid.

NOTE The “Day 1” mean values and the values of “Day 2” (to be submitted to the intra laboratory reproducibility variance Grubbs test) do not have a normal distribution [tests of Shapiro and Wilk and of Kolmogorov-Smirnov at 99 % confidence level].

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.4.4 Grubbs test, for intra laboratory reproducibility variance

The one-sided Grubbs' test is performed on the data corresponding to the "mean value of Day 1" and to the "value of Day 2". In this case, 2 × 14 values are tested:

Day	Laboratory	N mean values (%)
Mean values from Day 1	LAB 1	0,000 7
	LAB 2	0,001 2
	LAB 3	0,000 8
	LAB 4	0,000 6
	LAB 5	0,000 7
	LAB 6	0,001 0
	LAB 7	0,000 5
	LAB 8	0,000 9
	LAB 9	0,000 9
	LAB 10	0,000 9
	LAB 11	0,000 7
	LAB 12	0,001 0
	LAB 13	0,001 7
	LAB 14	0,000 8
Values from Day 2	LAB 1	0,000 8
	LAB 2	0,001 4
	LAB 3	0,000 7
	LAB 4	0,001 6
	LAB 5	0,000 7
	LAB 6	0,000 7
	LAB 7	0,000 4
	LAB 8	0,000 9
	LAB 9	0,000 8
	LAB 10	0,000 9
	LAB 11	0,000 7
	LAB 12	0,000 7
	LAB 13	0,001 3
	LAB 14	0,000 7
	Mean value	0,0008 7
	Standard deviation	0,0003 1
	Maximum value	0,0016 5
	Minimum value	0,0004 0
	Grubbs result for the maximum value	2,566
	Grubbs result for the minimum value	1,525
	Critical value [p = 28; 99 %] Critical value [p = 28; 95 %]	3,199 2,876

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test "by pairs" is then performed:

Day	Laboratory	N values (%)	Test for the 2 lowest values	Test for the 2 highest values
Mean values from Day 1	LAB 1	0,000 7		0,000 4
	LAB 2	0,001 2		0,000 5
	LAB 3	0,000 8	0,000 6	0,000 6
	LAB 4	0,000 6	0,000 7	0,000 7
	LAB 5	0,000 7	0,000 7	0,000 7
	LAB 6	0,001 0	0,000 7	0,000 7
	LAB 7	0,000 5	0,000 7	0,000 7
	LAB 8	0,000 9	0,000 7	0,000 7
	LAB 9	0,000 9	0,000 7	0,000 7
	LAB 10	0,000 9	0,000 7	0,000 7
	LAB 11	0,000 7	0,000 7	0,000 7
	LAB 12	0,001 0	0,000 7	0,000 7
	LAB 13	0,001 7	0,000 8	0,000 8
	LAB 14	0,000 8	0,000 8	0,000 8
Values from Day 2	LAB 1	0,000 8	0,000 8	0,000 8
	LAB 2	0,001 4	0,000 8	0,000 8
	LAB 3	0,000 7	0,000 9	0,000 9
	LAB 4	0,001 6	0,000 9	0,000 9
	LAB 5	0,000 7	0,000 9	0,000 9
	LAB 6	0,000 7	0,000 9	0,000 9
	LAB 7	0,000 4	0,000 9	0,000 9
	LAB 8	0,000 9	0,001 0	0,001 0
	LAB 9	0,000 8	0,001 0	0,001 0
	LAB 10	0,000 9	0,001 2	0,001 2
	LAB 11	0,000 7	0,001 3	0,001 3
	LAB 12	0,000 7	0,001 4	0,001 4
	LAB 13	0,001 3	0,001 6	
	LAB 14	0,000 7	0,001 7	
	Mean value	0,0008 7	0,0009 0	0,000 81
	Standard deviation	0,0003 1	0,0002 9	0,000 23
	Variance	0,000 000 093	0,000 000 086	0,000 000 051
	Grubbs result for the lowest pair		0,850 1	
	Grubbs result for the highest pair			0,507 3
	Critical value [*p* = 28; 99 %] Critical value [*p* = 28; 95 %]	0,475 9 0,547 0		

The “Day 1 mean value” from “LAB 13” (0,001 7 %) and the “Day 2” value from “LAB 4” (0,001 6 %) appear as stranglers, but NOT as outliers.

C.4.5 New table containing the set of laboratories having the same intra laboratory reproducibility variance for further tests

No outliers were found in C.4.4. The table from C.4.1 is still valid.

NOTE The “overall mean values of each set of data” (to be submitted to the inter laboratory reproducibility variance Grubbs test) do not have a normal distribution, excepted considering the test of Shapiro and Wilk at the 99 % level.

Nevertheless, it was decided to keep this example, in order to show how the subsequent tests are handled.

C.4.6 Grubbs test, for inter laboratory reproducibility variance

The one-sided Grubbs’ test is performed on the data corresponding to the “overall mean value of each set of remaining data”.

In this case, 14 values are tested:

Laboratory	N mean values (%)
LAB 1	0,000 7
LAB 2	0,001 3
LAB 3	0,000 7
LAB 4	0,000 9
LAB 5	0,000 7
LAB 6	0,000 9
LAB 7	0,000 5
LAB 8	0,000 9
LAB 9	0,000 8
LAB 10	0,000 9
LAB 11	0,000 7
LAB 12	0,000 9
LAB 13	0,001 5
LAB 14	0,000 7
Mean value	0,000 86
Standard deviation	0,000 26
Maximum value	0,001 53
Minimum value	0,000 47
Grubbs result for the maximum value	2,568
Grubbs result for the minimum value	1,512
Critical value [p = 14; 99 %] Critical value [p = 14; 95 %]	2,755 2,507

The overall mean value from “LAB 13” is a strangler, but NOT an outlier.

As the one-sided Grubbs test shows that there are no outliers in this case, the Grubbs test “by pairs” is then performed:

Laboratory	N mean values (%)	Test for the 2 lowest values	Test for the 2 highest values
LAB 1	0,000 7		0,000 5
LAB 2	0,001 3		0,000 7
LAB 3	0,000 7	0,000 7	0,000 7
LAB 4	0,000 9	0,000 7	0,000 7
LAB 5	0,000 7	0,000 7	0,000 7
LAB 6	0,000 9	0,000 7	0,000 7
LAB 7	0,000 5	0,000 8	0,000 8
LAB 8	0,000 9	0,000 9	0,000 9
LAB 9	0,000 8	0,000 9	0,000 9
LAB 10	0,000 9	0,000 9	0,000 9
LAB 11	0,000 7	0,000 9	0,000 9
LAB 12	0,000 9	0,000 9	0,000 9
LAB 13	0,001 5	0,001 3	
LAB 14	0,000 7	0,001 5	
Mean value	0,000 86	0,0009 1	0,000 77
Standard deviation	0,000 26	0,0002 5	0,000 13
Variance	0,000 000 068	0,000 000 060	0,000 000 016
Grubbs result for the lowest pair		0,748 6	
Grubbs result for the highest pair			0,199 7
Critical value [*p* = 14; 99 %] Critical value [*p* = 14; 95 %]	0,220 8 0,311 2		

The overall mean values from “LAB 2” and from “LAB 13” are Grubbs outliers as “a pair”.

C.4.7 New table containing the set of laboratories having the same inter laboratory reproducibility variance for further evaluations

The data from the retained laboratories are edited in a new table:

Laboratory	Day 1	Day 2
LAB 1	0,000 7	0,000 8
	0,000 7	
LAB 3	0,000 7	0,000 7
	0,000 8	
LAB 4	0,000 5	0,001 6
	0,000 6	
LAB 5	0,000 5	0,000 7
	0,000 8	
LAB 6	0,001 0	0,000 7
	0,001 0	
LAB 7	0,000 5	0,000 4
	0,000 5	
LAB 8	0,000 9	0,000 9
	0,000 8	
LAB 9	0,000 9	0,000 8
	0,000 8	
LAB 10	0,000 9	0,000 9
	0,000 8	
LAB 11	0,000 7	0,000 7
	0,000 7	
LAB 12	0,001 0	0,000 7
	0,000 9	
LAB 14	0,000 7	0,000 7
	0,000 8	

C.5 General remarks about the examples shown

It may appear illogical having presented examples with populations that failed to the normality tests at different stages. Nevertheless, as the different notes edited all along the examples explain, such presentations were kept for “didactic purposes” concerning the way how the sequences of the different tests should be handled.

It also should be underlined that:

— For the case of Nitrogen determination, if we consider the data issued from the corresponding Working Group report, “LAB 4” appeared as an outlier (or a strangler) for six levels (samples), whilst a total of eight levels were under consideration. This report did not present the Mendel's statistics representing the data treated, but we may think that the lack of accuracy presented by “LAB 4” would be clearly detected if this kind of evaluation had been performed. The presence of the data from “LAB 4” also conducts to the failure of the normality tests. It appears quite obvious that in such case an entire second statistical evaluation would have been carried out, after having removed ALL the data from the laboratory labelled “LAB 4”.

— For the case of Chromium determination, even if the performances of “LAB 3” were “acceptable” it was this laboratory that appeared to have the worst position when considering, at least, the Mendel's within-laboratory consistency statistics “k”.

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