TECHNICAL REPORT

ISO/TR 21074

First edition
2016-10-15

Application of ISO 5725 for the determination of repeatability and reproducibility of precision tests performed in standardization work for chemical analysis of steel

Application de la norme ISO 5725 pour la détermination de la répétabilité et la reproductibilité des essais de précision réalisés en travaux de normalisation pour l'analyse chimique de l'acier

Reference number
ISO/TR 21074:2016(E)

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Contents

Page

Foreword

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The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Application of ISO 5725 for the determination of repeatability and reproducibility of precision tests performed in standardization work for chemical analysis of steel

1 Scope

This document describes how to determine the repeatability and reproducibility of precision tests performed within standardization work using the chemical analysis method. Specifically, this document explains the procedure for calculating precision, using precision test data of ISO 5725-3:1994, Table D.2 for the precision test in ISO 9647:1989 as an example.

The procedure of the international test for determining precision is described in ISO 5725-2 and ISO 5725-3.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Precision test

4.1 Structure of the precision test

The structure of the precision test normally used within standardization work using chemical analysis is a 3-factor, staggered-nested structure, as shown in Figure 1.

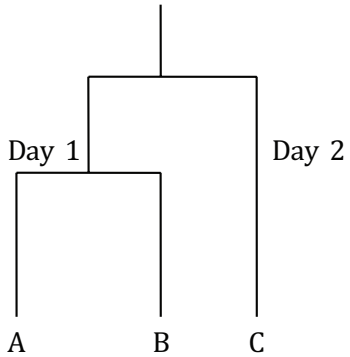


Figure 1 — Structure of the precision test

a) Both A and B (Day 1) are obtained under repeatability where independent test results are obtained with the same method on identical items in the same laboratory by the same operator using the same equipment within short intervals of time.

b) C (Day 2) is obtained under time-different intermediate precision conditions, except for the time factor. The measurement is performed by the same operator and, in addition, the measurements at a given level are performed using the same sample and equipment throughout.

4.2 Homogeneity of samples

For a precision test it is important to use homogeneous samples. Therefore, it is necessary to control the homogeneity of the samples selected for each precision test, if the samples are not certified reference materials, before starting a test in order to be sure that the heterogeneity level of the sample can be included in the expected precision values.

4.3 Number of laboratories and number of levels

In principle, the number of laboratories that participate in an international cooperative test is decided on the basis of the required precision. As this approach is often difficult to implement, the practical rule typically followed is the selection of 8 to 15 (or more) laboratories see ISO 5725-1:1994, 6.3.4, preferably in 5 countries. The number of levels depends on the range and scope of the method to be tested. A minimum of two levels by decade with the scheme (for example, 1–10) is required, and in the case of limited application ranges, three or more levels by decade (for example, 1–2–5–10) can be selected.

NOTE Fully-nested experiments offer higher reliability of repeatability than staggered-nested experiments. However, it will not improve the reliability of reproducibility significantly. From the standpoint of improving reliability, it is effective to increase the number of participating laboratories.

5 Representation of the experimental results

5.1 General

First, on the basis of precision test results, prepare the following tables and graphs.

5.2 Table of results and number of decimal places

Prepare a list of precision data.

In the list of data, the number of decimal places is the number required in the experiment plus one according to the convenor's requirement.

Table 1 shows an example of a list of data.

The data obtained by laboratory i are indicated by y_{ij} (j = 1, 2, 3).

The symbol p represents the number of laboratories participating in the experiment. (It should be noted that the number changes if outliers are deleted.)

Table 1 — Original results

Lab. no.	Day 1		Day 2
	A	B	C
1	y11	y12	y13
—	—	—	—
i	yi1	yi2	yi3
—	—	—	—
p	yp1	yp2	yp3

5.3 Graphical representation of the data

5.3.1 General

All data can be evaluated by graphical representation just to get an overview of the data population distribution. If there are laboratories which have obviously erroneous values for several levels, eliminating those laboratories as an outlier may be considered if deemed necessary.

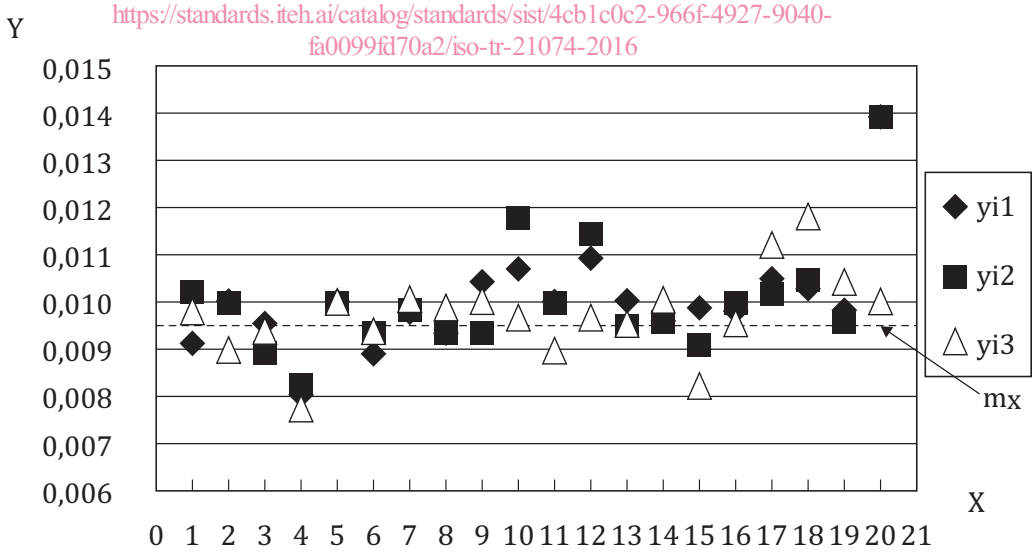
5.3.2 Data plot

Draw a graph for each of the levels by plotting the data as follows.

a) For each of the laboratories in Table 1, plot Day 1 to 1 (= yi1), Day 1 to 2 (= yi2) and Day 2 (= yi3) using different symbols.

b) Indicate the average m_x for each level.

An example of the graph for the original results is shown in Figure 2.



Key

X laboratory no.

Y contents % (mass fraction)

Figure 2 — Original results

6 Statistical evaluation

The general flow chart of the statistical evaluation is shown in Figure 3.

Perform Cochran's test and Grubbs' test following the procedure shown below to detected the outliers and delete them. The flow chart diagram of the tests is shown in Figure 4.

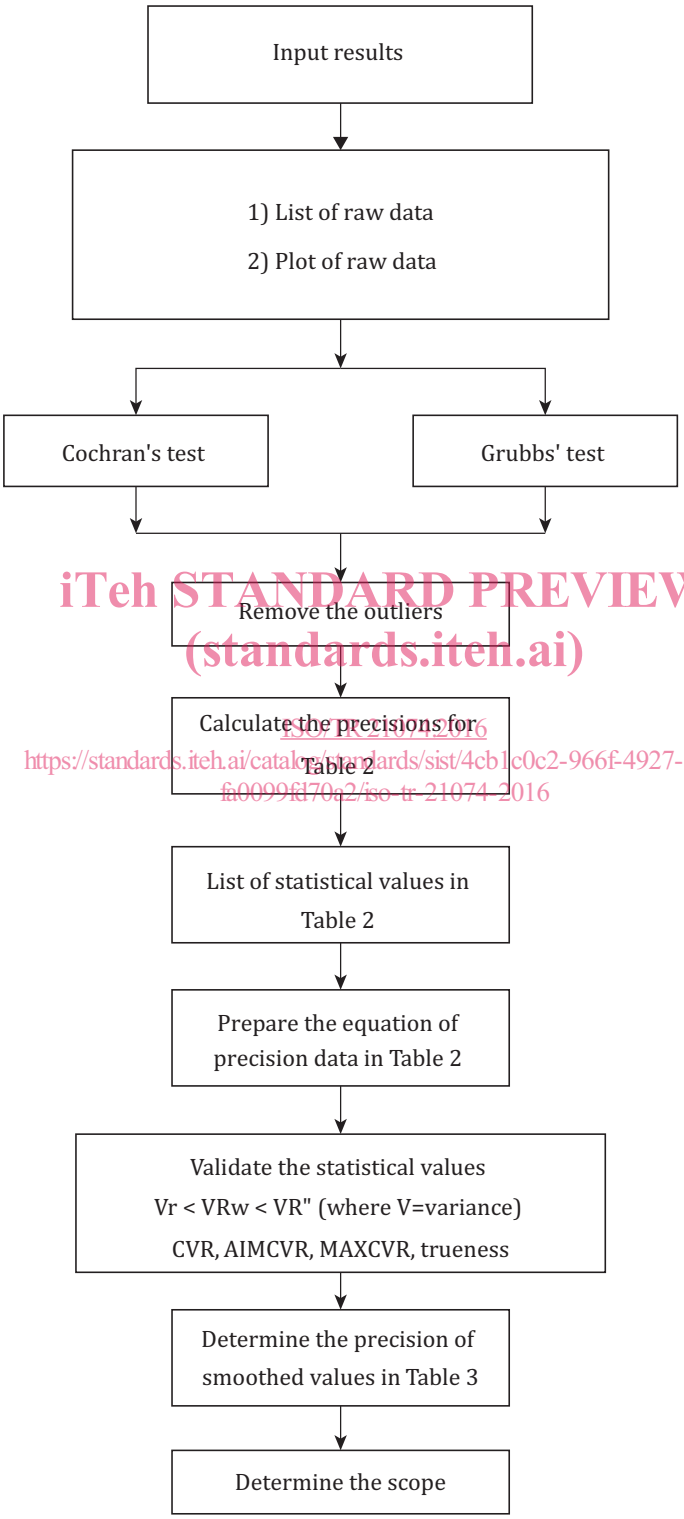


Figure 3 — Flow for determining the precision

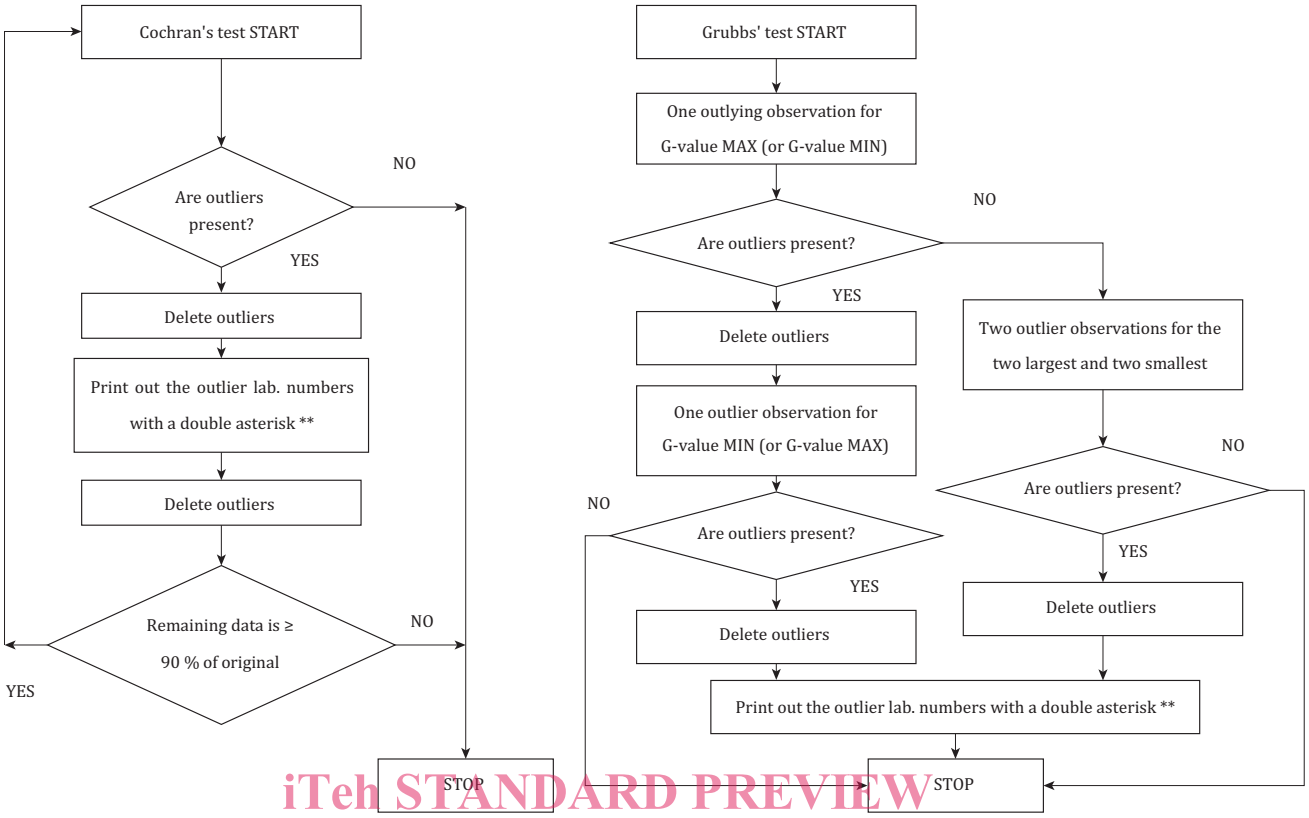


Figure 4 — Flow diagram of the Cochran's test and Grubbs' test

6.1 Cochran's test

See ISO 5725-2:1994, 7.3.3.

The purpose of the Cochran's test is to evaluate the interlaboratory repeatability variance. For that purpose, the intralaboratory repeatability variance is calculated and compared with those of other laboratories.

For each level j, perform the following calculations on each test data set. The test data sets are (A, B) and [(A+B)/2, C].

a) Obtain the standard deviation:

$$S_{ij} = \left| y_{ij1} - y_{ij2} \right| / \sqrt{2}$$

b) Calculate the C-value:

$$C = \frac{S_{\max}^2}{\sum_{i=1}^{p} S_i^2}$$

where

i is the identifier for a certain lab;

j is the identifier for a certain level;

p is the number of laboratories of level j (note that the number, p, changes if outliers are deleted);

$S_{\max}$ is the highest standard deviation in the set of level j.

c) Compare the calculated value with the value for n = 2 in the critical values table (see ISO 5725-2:1994, Table 4).

d) If the calculated value is larger than 1 % critical value, assume it is an outlier and delete the corresponding data. Then, repeat steps a) to c) for the remaining data.

e) Finish the test either when no outliers are detected or the remaining data are equal to or not less than 90 % of the original data.

NOTE A piece of statistical data greater than 1 % or 5 % of the critical value is called an "outlier" and "straggler", respectively.

6.2 Grubbs' test

6.2.1 General

See ISO 5725-2:1994, 7.3.4.

The purpose of the Grubbs' test is to evaluate the between-laboratory consistency. For that purpose, the cell average for each laboratory is obtained and evaluated in terms of the deviation from the overall average.

Using (A+B+C)/3 as the test data, perform the following calculations for each level j.

NOTE The symbols used in this clause are the same as those in 6.1

a) Obtain the average value $x_i = \bar{y}_{ij}$ of A-B-C.

b) Arrange the average values $x_i = \bar{y}_{ij}$ in ascending order.

$x_i \left(i = 1, 2, \ldots p\right)$

NOTE The number, p, changes if outliers are removed.

d) Obtain the unbiased variance for $x_i = \bar{y}_{ij}$:

$$\bar{x} = \frac{1}{p}\sum_{i=1}^{p} x_i \qquad S = \sqrt{\frac{1}{p-1}\sum_{i=1}^{p}(x_i - \bar{x})^2}$$

6.2.2 Grubbs' test for one outlier observation

See ISO 5725-2:1994, 7.3.4.1.

a) Calculate the following G-values and compare them with the appropriate value in the table of critical values (see ISO 5725-2:1994, Table 5). If the calculated value is larger than 1 % critical value, assume it is an outlier.

   1) Test of the maximum value: $G_p = (x_p - \bar{x})/S$

   2) Test of the minimum value: $G_1 = (\bar{x} - x_1)/S$

b) If in a) above the maximum value (minimum value) is an outlier, remove it and apply the Grubb's test to the minimum value (maximum value).

c) Finish the test when no outliers are detected in steps a) and/or b). When no outliers are detected, conduct a further test for two outlier observations (6.2.2).

6.2.3 Grubbs' test for two outlier observations

See ISO 5725-2:1994, 7.3.4.2.

If in the above Grubbs' test [a) to c)] neither the maximum value nor the minimum value is an outlier, calculate the following G-values and compare them with the appropriate value in the table of critical values (see ISO 5725-2:1994, Table 5). If the calculated value is *smaller*, assume it is an outlier.

a) Test of the two largest observations: $G = S^2_{p-1,p}/S^2_0$

b) Test of the two smallest observations: $G = S^2_{1,2}/S^2_0$

where

$$S_0^2 = \sum_{i=1}^{p} (x_i - \bar{x})^2$$

$$S_{p-1,p}^2 = \sum_{i=1}^{p-2} (x_i - \bar{x}_{p-1,p})^2$$

$$\bar{x}_{p-1,p} = \frac{1}{p-2} \sum_{i=1}^{p-2} x_i$$

$$S_{1,2}^2 = \sum_{i=3}^{p} (x_i - \bar{x}_{1,2})^2$$

$$\bar{x}_{1,2} = \frac{1}{p-2} \sum_{i=3}^{p} x_i$$