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Accuracy (trueness and precision) of measurement methods and results —

Part 4: Basic methods for the determination of the trueness of a standard measurement method

Exactitude (justesse et fidélité) des résultats et méthodes de mesure —

Partie 4: Méthodes de base pour la détermination de la justesse d'une méthode de mesure normalisée

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Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) , see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 69, Subcommittee SC 6, *Measurement methods and results*.

This second edition cancels and replaces the first edition (ISO 5725-4:1994), which has been technically revised.

The main changes compared to the previous edition are as follows:

— clearly recognizing the requirements of the accepted reference values used in bias evaluation experiments and introducing the uncertainties of the accepted reference values,

— changing examples with a currently used measurement method.

A list of all parts in the ISO 5725 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

ISO 5725 uses two terms, “trueness” and “precision”, to describe the accuracy of a measurement method. “Trueness” refers to the closeness of agreement between the expectation of a measurement result and a true value. "Precision" refers to the closeness of agreement between independent measurement results obtained under stipulated conditions.

General consideration of these quantities is given in ISO 5725-1 and so is not repeated in this document. ISO 5725-1 should be read in conjunction with all other parts of ISO 5725, including this document, because it gives the underlying definitions and general principles.

The “trueness” of a measurement method is of interest when it is possible to conceive of a true value for the property being measured. Although the true value cannot be known exactly, it can be possible to have an accepted reference value for the property being measured; for example, if suitable reference materials or measurement standards are available, or if the accepted reference value can be established by reference to another measurement method or by preparation of a known sample. The trueness of the measurement method can be investigated by comparing the accepted reference value with the level of the results given by the measurement method. Trueness is normally expressed in terms of bias. Bias can arise, for example, in chemical analysis if the measurement method fails to extract all of an element, or if the presence of one element interferes with the determination of another.

Two measures of trueness are of interest and both are considered in this document.

a) Bias of the measurement method: where there is a possibility that the measurement method can give rise to a bias, which persists wherever and whenever the measurement is done, then it is of interest to investigate the “bias of the measurement method”. This requires an experiment involving many laboratories.

b) Laboratory bias: measurements within a single laboratory can reveal the “laboratory bias” (as defined in ISO 5725-1). If it is proposed to undertake an experiment to estimate laboratory bias, then it should be realized that the estimate is valid only at the time of the experiment and at the investigated level(s) for the property. Further regular testing is required to show that the laboratory bias does not vary; the method described in ISO 5725-6 can be used for this.

Accuracy (trueness and precision) of measurement methods and results —

Part 4: Basic methods for the determination of the trueness of a standard measurement method

1 Scope

1.1 This document

— specifies basic methods for estimating the bias of a measurement method and the laboratory bias when a measurement method is applied;

— provides a practical approach of a basic method for routine use in estimating the bias of measurement methods and laboratory bias;

— provides a brief guidance to all personnel concerned with designing, performing or analysing the results of the measurements for estimating bias.

1.2 It is concerned exclusively with measurement methods which yield measurements on a continuous scale and give a single value as the measurement result, although the single value can be the outcome of a calculation from a set of observations.

1.3 This document applies when the measurement method has been standardized and all measurements are carried out according to that measurement method.

NOTE In ISO/IEC Guide 99:2007(VIM), "measurement procedure" (2.6) is an analogous term related to the term "measurement method" used in this document.

1.4 This document applies only if an accepted reference value can be established to substitute the true value by using the value, for example:

— of a suitable reference material;

— of a suitable measurement standard;

— referring to a suitable measurement method;

— of a suitable prepared known sample.

1.5 This document applies only to the cases where it is sufficient to estimate bias on one property at a time. It is not applicable if the bias in the measurement of one property is affected by the level of any other property (i.e. it does not consider interferences by any influencing quantity). Comparison of the trueness of two-measurement methods is considered in ISO 5725-6.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 3534-1, *Statistics — Vocabulary and symbols — Part 1: General statistical terms and terms used in probability*

ISO 3534-2, *Statistics — Vocabulary and symbols — Part 2: Applied statistics*

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

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO Guide 30, *Reference materials — Selected terms and definitions*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3534-1, ISO 3534-2, ISO 5725-1 and ISO Guide 30 apply.

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

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

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

4 Symbols

A	Factor used to calculate the measurement uncertainty of an estimate
B	Laboratory component of bias
C, C', C''	Test statistics
C_{crit}, C'_{crit}, C''_{crit}	Critical values for statistical tests
e	Random error occurring in every measurement under repeatability conditions
G	Grubbs' test statistic
h	Mandel's between-laboratory consistency test statistic
k	Mandel's within-laboratory consistency test statistic
n	Number of measurement results obtained in one laboratory at one level of the property being measured (i.e. per cell)
p	Number of laboratories participating in the interlaboratory experiment
P	Probability
s	Estimate of a standard deviation
u	Standard measurement uncertainty; quantile of the standard normal distribution
y	Measurement result
$\bar{y}$	Average of the measurement results
$\bar{\bar{y}}$	Grand mean of the measurement results
α	Significance level (α is assumed to be 0,05 in this document)

β	Type II error probability
Φ	Cumulative distribution function of the standard normal distribution
γ	Ratio of the reproducibility standard deviation to the repeatability standard deviation (σ_R/σ_r)
δ	Bias of the measurement method under investigation
$\hat{\delta}$	Estimate of the bias of the measurement method under investigation
Δ	Laboratory bias
$\hat{\Delta}$	Estimate of the laboratory bias
μ	Accepted reference value of a property being measured
ν	Number of degrees of freedom
σ	True value of a standard deviation
$\chi^2_P(\nu)$	P-quantile of the χ^2-distribution with ν degrees of freedom

Subscripts

i	Identifier for a participating laboratory; identifier for an individual laboratory (inner laboratory)
k	Identifier for a particular measurement result from a laboratory
L	Between-laboratory (interlaboratory)
m	Identifier for detectable bias
P	Probability
r	Repeatability
R	Reproducibility
y	Identifier for the measurement result
0	Identifier for the accepted reference value

5 Determination of the bias of a standard measurement method by an interlaboratory experiment

5.1 Experimental design considerations

5.1.1 Objective

The objective of the experiment is to estimate the value of the bias of the measurement method and to determine when it is statistically significant. When the bias is found to be statistically insignificant, then the objective is to determine the maximum absolute value of bias that can remain, with a certain probability, undetected by the results of the experiment.

5.1.2 Layout of the experiment

The layout of the experiment is almost the same as that for a precision experiment, as described in ISO 5725-2. The differences are

— the number of participating laboratories and the number of measurement results shall also satisfy the requirements given in 5.3, and

— there is an additional requirement, given in 5.4, to use an accepted reference value of the property being measured.

5.1.3 Cross-references to ISO 5725-1 and ISO 5725-2

Requirements on experimental design given in ISO 5725-1 and ISO 5725-2 apply. When reading ISO 5725-1 and ISO 5725-2 in this context, "trueness" shall be inserted in place of "precision" or "repeatability and reproducibility" as appropriate.

5.2 The statistical model

The basic model of a measurement result, y, can be expressed as

$$y=\mu+\delta+B+e \tag{1}$$

where

μ is the accepted reference value of a property being measured;

δ is the bias of the measurement method under investigation;

B is the laboratory component of bias;

e is the random error occurring in every measurement under repeatability conditions.

NOTE In this document, bias is evaluated at one level at a time; for convenience, the index j, defined in ISO 5725-1, for the level of property has been omitted throughout.

When all of measurement results are obtained according to the requirements in 5.3 and 5.4 from the sufficient number of participant laboratories and sufficient number of measurements under repeatability conditions in each laboratory by using the same measurement method, the bias of the measurement method, at each level of the property, is estimated by

$$\hat{\delta}=\bar{\bar{y}}-\mu \tag{2}$$

where

$\hat{\delta}$ is an estimate of the bias of the measurement method under investigation;

$\bar{\bar{y}}$ is the grand mean of the measurement results from all participant laboratories;

μ is the accepted reference value of the property being measured.

5.3 Required number of laboratories and measurements

The number of laboratories and the number of measurement results required at each laboratory are interdependent. Guidance on selecting these numbers is given below. Although it is assumed that the laboratory biases can be regarded as draws from an approximately normal distribution, in practice the guidance is appropriate for most unimodal distributions.

For the results of an experiment to be able to detect with a high probability a predetermined maximum absolute value of bias, δ_m, the following formula shall be satisfied:

$$A\sigma_R \leq \frac{\delta_m}{1,84} \tag{3}$$

where

A is a factor used in calculating the measurement uncertainty of an estimate of bias (see below);

σ_R is the reproducibility standard deviation of the measurement method;

δ_m is the predetermined maximum absolute value of bias that the experimenter wishes to detect from the results of the experiment;

1,84 is a derived factor (see Annex A).

In Formula (3), A is a function of the number of laboratories, the number of measurement results in each laboratory, the reproducibility standard deviation of the measurement method and the measurement uncertainty of the accepted reference value. A is given by

$$A = 1,96\sqrt{A_0^2 + A_y^2} = 1,96\sqrt{\frac{u^2(\mu)}{\sigma_R^2} + \frac{n(\gamma^2 - 1) + 1}{\gamma^2 pn}} \tag{4}$$

where

1,96 is the 0,975-quantile of the standard normal distribution (see Annex A);

A_0 is the ratio of the standard measurement uncertainty of the accepted reference value to the reproducibility standard deviation of the measurement method;

A_y is the ratio of the standard deviation of the grand mean in this experiment to the reproducibility standard deviation of the measurement method;

$u(\mu)$ is the standard measurement uncertainty of the accepted reference value;

n is the number of measurement results in each laboratory;

p is the number of participating laboratories;

γ is the ratio of the reproducibility standard deviation to the repeatability standard deviation.

In Formula (4), A_0, A_y and γ are given respectively by

$$A_0 = u(\mu)/\sigma_R \tag{5}$$

$$A_y = \sqrt{\frac{n(\gamma^2 - 1) + 1}{\gamma^2 pn}} \tag{6}$$

$$\gamma = \sigma_R/\sigma_r \tag{7}$$

where σ_r is the repeatability standard deviation of the measurement method.

If the measurement uncertainty of the accepted reference value is small enough to be neglected, implying $A_0 \leq 0{,}3A_y$ (i.e. $u(\mu) \leq 0{,}3A_y\sigma_R$), Formula (4) may be simplified to

$$A = 1{,}96A_y \tag{8}$$

The values of A calculated by Formula (8) are given in Table 1.

Ideally, the choice of the combination of the number of laboratories and the number of replicate measurement results per laboratory should satisfy the requirement described by Formula (3), with the δ_m value predetermined by the experimenter. However, for practical reasons, the choice of the number of laboratories is usually a compromise between the availability of resources and the desire to reduce the value of δ_m to a satisfactory extent. If the reproducibility of the measurement method is poor, then it is not practical to achieve a high degree of certainty in the estimate of the bias. When σ_R is larger than σ_r (i.e. γ is larger than 1) as is often the case, little is to be gained by obtaining more than $n = 2$ measurement results per laboratory per level.

Table 1 — Values of A, the factor used in calculating the measurement uncertainty of an estimate of bias in the case when the measurement uncertainty of the accepted reference value is small enough to be neglected

No. of laboratories	Value of A calculated by Formula (8)								
	$\gamma = 1$			$\gamma = 2$			$\gamma = 5$		
p	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$	$n = 2$	$n = 3$	$n = 4$
5	0,62	0,51	0,44	0,82	0,80	0,79	0,87	0,86	0,86
10	0,44	0,36	0,31	0,58	0,57	0,56	0,61	0,61	0,61
15	0,36	0,29	0,25	0,47	0,46	0,46	0,50	0,50	0,50
20	0,31	0,25	0,22	0,41	0,40	0,40	0,43	0,43	0,43
25	0,28	0,23	0,20	0,37	0,36	0,35	0,39	0,39	0,39
30	0,25	0,21	0,18	0,33	0,33	0,32	0,35	0,35	0,35
35	0,23	0,19	0,17	0,31	0,30	0,30	0,33	0,33	0,33
40	0,22	0,18	0,15	0,29	0,28	0,28	0,31	0,31	0,31

5.4 Requirements of the accepted reference value

5.4.1 Approaches to assigning the accepted reference value

The accepted reference value of the property of interest, μ, shall be reliable and metrologically traceable to an accepted reference by which the true value can be substituted. It refers to the value carried by the material used in this experiment, which was either assigned in another independent study, such as the characterization of the reference material, the calibration of the measurement standard by using suitable calibration procedures and competent laboratories, the assignment by other measurement method (preferably a reference measurement method), or calculated from the property values of the materials used for preparation of the known sample.

NOTE Guidance for the characterization and use of reference materials is given in ISO Guide 35 and ISO Guide 33, respectively. Refer to the definition for other measurement standards in ISO/IEC Guide 99 (VIM).

5.4.2 Materials used in the experiment

5.4.2.1 The material used in the experiment, whether purchased or prepared, can be a reference material, a measurement standard or a prepared known sample; it shall have the same property as that the standard measurement method is intended to be applied to, e.g. concentration.

5.4.2.2 The value of the property of interest carried by the material, which has been assigned by any approach listed in 5.4.1, shall be appropriate to the range of values at which the standard measurement

method is intended to be applied. In some cases, it is important to include a series of the materials, each corresponding to a different level of the property, preferably covering the range of values of the measurement method as completely as possible, because the bias of the measurement method can be different at different levels of the property.

5.4.2.3 The material should have a matrix as close as possible to that to be subjected to the standard measurement method, e.g. carbon in coal or carbon in steel.

5.4.2.4 The quantity of the materials shall be sufficient for the entire experimental programme, including some in reserve if this is considered necessary, such as for contingencies in transportation and potential re-measurements.

5.4.2.5 Wherever possible, the materials should have stable property values throughout the experiment. In the case of unstable materials, special instructions on transportation, storage and/or treatment shall be specified, so that the requirements in 5.4.3 can be achieved.

5.4.2.6 Where subdivision of the unit of the material occurs prior to distribution, it shall be performed with care to avoid the introduction of any additional error. Relevant International Standards and other documents on sample division should be consulted. The units shall be selected on a random basis for distribution. If the measurement process is non-destructive, it is possible to give all the laboratories in the interlaboratory experiment the same unit of the material, but this can extend the timeframe of the experiment.

5.4.2.7 In principle, the material should be adequately homogeneous, i.e. it should have an acceptable level of heterogeneity. When a material has to be homogenized, this shall be done in the manner most appropriate for that material. When the material to be measured is not sufficiently homogeneous, it is important to prepare the samples in the manner specified in the method, preferably starting with one batch of commercial material for each level of the property value. In particular, the known samples prepared by mixing materials with different known levels of property values in specified proportions, or by spiking a specified proportion of a substance to a matrix material, shall be quantified for their homogeneity, so that the requirements in 5.4.3 can be achieved.

5.4.3 Requirements of measurement uncertainty of the accepted reference value

5.4.3.1 The standard measurement uncertainty of the accepted reference value, cited or derived from that in relevant documents accompanying the material or estimated for this experiment, shall be controlled to be as low as possible. If it is lower than $0{,}3A_y\sigma_R$, the effect of the accepted reference value on the measurement uncertainty of the estimate of the bias may be neglected. If it is higher than $A_y\sigma_R$, two strategies should be considered:

— increasing p or both p and n, so that the value of A is reduced to such a level that the predetermined value of bias can be detected with a high probability;

— choosing other materials which carry an accepted reference value meeting this requirement.

5.4.3.2 The standard measurement uncertainty of the accepted reference value consists of, in principle, components arising from characterization (or calibration, or preparation) procedures, heterogeneity and instability, and the measurement uncertainty arising from bias. However, for historical reasons, sometimes the uncertainties arising from heterogeneity, instability and/or bias were not included (maybe separately stated) in the certificate of reference material or measurement standard. They should be estimated by additional studies (or combined with the stated measurement uncertainty), unless there is reliable evidence that they are negligible.

5.4.3.3 Contribution of the heterogeneity to the measurement uncertainty can depend on the mass or volume used in the measurement. If the heterogeneity measurement uncertainty is the dominant component of the measurement uncertainty of the accepted reference value, the mass or volume used

in the homogeneity check experiment shall be no larger than that to which the measurement method is applied. Otherwise the heterogeneity measurement uncertainty shall be re-assessed based on the latter mass or volume, and the measurement uncertainty of the accepted reference value shall be re-calculated.

5.5 Carrying out the experiment

5.5.1 Evaluation of precision

5.5.1.1 The precision experiment shall be carried out according to ISO 5725-2.

5.5.1.2 The measurement results shall be treated as described in ISO 5725-2, where the precision of the measurement method is expressed in terms of s_r (estimate of the repeatability standard deviation) and s_R (estimate of the reproducibility standard deviation).

5.5.1.3 The estimate s_r^2 of the repeatability variance and the estimate s_R^2 of the reproducibility variance are calculated by Formulae (9) to (13), provided that the number (n) of measurement results in each laboratory is equal. If this is not true, the formulae for s_r and s_R given in ISO 5725-2 shall be used.

$$s_r^2 = \frac{1}{p}\sum_{i=1}^{p} s_i^2 \tag{9}$$

$$s_R^2 = \frac{1}{p-1}\sum_{i=1}^{p}(\bar{y}_i - \bar{\bar{y}})^2 + \left(1 - \frac{1}{n}\right)s_r^2 \tag{10}$$

with

$$s_i^2 = \frac{1}{n-1}\sum_{k=1}^{n}(y_{ik} - \bar{y}_i)^2 \tag{11}$$

$$\bar{y}_i = \frac{1}{n}\sum_{k=1}^{n} y_{ik} \tag{12}$$

$$\bar{\bar{y}} = \frac{1}{p}\sum_{i=1}^{p}\bar{y}_i \tag{13}$$

where s_i^2 and $\bar{y}_i$ are respectively the variance and the average of n measurement results y_{ik} obtained in laboratory i.

Outliers shall be investigated according to the procedures given in ISO 5725-2.

5.5.2 Check of precision

5.5.2.1 If the repeatability standard deviation and the reproducibility standard deviation of the standard measurement method have not been previously determined in accordance with ISO 5725-2, s_r and s_R are considered to be the best estimates of those.

5.5.2.2 If the repeatability standard deviation of the standard measurement method, σ_r, has been determined in accordance with ISO 5725-2, s_r^2 can be assessed by computing the ratio

$$C = s_r^2 / \sigma_r^2 \tag{14}$$

The test statistic C is compared with the critical value

$$C_{\text{crit}} = \chi^2_{(1-\alpha)}(\nu)/\nu$$

where $\chi^2_{(1-\alpha)}(\nu)$ is the $(1 - \alpha)$-quantile of the χ^2 distribution with $\nu = p(n - 1)$ degrees of freedom.

a) If $C \leq C_{\text{crit}}$: s_r^2 is not significantly larger than σ_r^2.

b) If $C > C_{\text{crit}}$: s_r^2 is significantly larger than σ_r^2.

In the former case, the repeatability standard deviation, σ_r, is to be used for the assessment of the bias of the measurement method.

In the latter case, it is necessary to investigate the causes of the discrepancy and possibly to repeat the experiment prior to proceeding further.

NOTE Other statistical techniques, such as two-side F-test, have been suggested for the check of repeatability and reproducibility standard deviation, it is duty of the panel (refer to Clause 7) to decide which technique is suitable.

5.5.2.3 If the reproducibility standard deviation, σ_R, and the repeatability standard deviation, σ_r, of the standard measurement method have been determined in accordance with ISO 5725-2, s_R can be assessed indirectly by computing the ratio

$$C' = \frac{s_R^2 - (1-1/n)s_r^2}{\sigma_R^2 - (1-1/n)\sigma_r^2} \tag{15}$$

The test statistic C' is compared with the critical value

$$C'_{\text{crit}} = \chi^2_{(1-\alpha)}(\nu)/\nu$$

where $\chi^2_{(1-\alpha)}(\nu)$ is the $(1 - \alpha)$-quantile of the χ^2 distribution with $\nu = p - 1$ degrees of freedom.

a) If $C' \leq C'_{\text{crit}}$: $s_R^2 - (1-1/n)s_r^2$ is not significantly larger than $\sigma_R^2 - (1-1/n)\sigma_r^2$.

b) If $C' > C'_{\text{crit}}$: $s_R^2 - (1-1/n)s_r^2$ is significantly larger than $\sigma_R^2 - (1-1/n)\sigma_r^2$.

In the former case, the repeatability standard deviation, σ_r, and the reproducibility standard deviation, σ_R, are to be used for the assessment of the trueness of the measurement method.

In the latter case, a careful examination of the working conditions of each laboratory shall be carried out before the assessment of the bias of the standard measurement method is undertaken. As a result, the experiment can have to be repeated to yield the expected precision values.

NOTE It can appear that some laboratories did not use the required equipment or did not work according to the specified conditions. In chemical analysis, problems can arise from, for example, insufficient control of temperature, moisture, presence of contaminants, etc.

5.5.3 Estimation of the bias of the standard measurement method

5.5.3.1 The estimate of the bias is given by

$$\hat{\delta} = \bar{\bar{y}} - \mu \tag{16}$$

where $\hat{\delta}$ can be positive or negative.

5.5.3.2 The variation of the estimate of the bias of the measurement method is due to the variation in the results of the measurement process and the variation of the accepted reference value. In the case of known precision values, the standard deviation of the estimate of the bias is

$$\sigma_{\hat{\delta}} = \sqrt{\frac{\sigma_R^2 - (1 - 1/n)\sigma_r^2}{p} + u^2(\mu)} \tag{17}$$

or, in the case of unknown precision values, as

$$s_{\hat{\delta}} = \sqrt{\frac{s_R^2 - (1 - 1/n)s_r^2}{p} + u^2(\mu)} \tag{18}$$

5.5.3.3 An approximate 0,95 confidence interval for the bias of the measurement method can be computed as

$$\left[\hat{\delta} - A\sigma_R,\ \hat{\delta} + A\sigma_R\right] \tag{19}$$

where A is as given in Formula (4). If σ_R is unknown, its estimate s_R shall be used instead, and A shall be computed with $\gamma = s_R/s_r$ rather than Formula (7).

If this confidence interval contains the value zero, the bias of the measurement method is insignificant at the significance level $\alpha = 0{,}05$; otherwise it is significant.

5.5.4 Example

An example for the bias assessment by an inter-laboratory experiment is given in Annex B.

6 Determination of the laboratory bias of one laboratory using a standard measurement method

6.1 Experimental design considerations

6.1.1 Objective

The objective of the experiment is to estimate the value of the bias of a particular laboratory and to determine if it is statistically significant. If the bias is found to be statistically insignificant, then the objective is to determine the value of the maximum bias that can remain, with a certain probability, undetected by the results of the experiment.

6.1.2 Layout of the experiment

6.1.2.1 An interlaboratory precision experiment, in accordance with ISO 5725-2, has established the repeatability standard deviation of the method before this experiment for estimating the laboratory bias.

6.1.2.2 The experiment shall conform strictly to the standard method and measurements shall be carried out under repeatability conditions. If the repeatability of the measurement method is poor, then it cannot be practical to achieve small measurement uncertainty in the estimate of the laboratory bias.

6.1.2.3 The layout of the experiment consists of the measurements required of one laboratory in a precision experiment as described in ISO 5725-2. Apart from the restriction to a single laboratory, the only substantial difference is the additional requirement to use an accepted reference value. The number of measurement results shall satisfy the requirements given in 6.3.

6.1.3 Cross-references to ISO 5725-1 and ISO 5725-2

When reading ISO 5725-1 and ISO 5725-2 in this context, "trueness" should be inserted in place of "precision" or "repeatability and reproducibility" as appropriate, in ISO 5725-2, the number of laboratories is p = 1, and it can be convenient for one person to combine the roles of "executive" and "supervisor".

6.2 The statistical model

The laboratory bias, Δ, is given by

$$\Delta = \delta + B \tag{20}$$

So, the model can be written

$$y = \mu + \Delta + e \tag{21}$$

6.3 Number of measurement results

The measurement uncertainty of the estimate of the laboratory bias depends on the repeatability of the measurement method, on the number of measurement results obtained and on the measurement uncertainty of the accepted reference value used.

For the results of an experiment to be able to detect with a high probability (see Annex A), a predetermined absolute value of bias and the number of measurement results shall satisfy the following formula:

$$A_i \sigma_r \leq \frac{\Delta_m}{1{,}84} \tag{22}$$

where

A_i is a factor used in calculating the measurement uncertainty of an estimate of laboratory bias;

σ_r is the repeatability standard deviation of the measurement method, and

Δ_m is the predetermined absolute value of laboratory bias that the experimenter wishes to detect from the results of the experiment;

1,84 is a derived factor (see Annex A).

In Formula (22), A_i is a function of the number of measurement results and the measurement uncertainty of the accepted reference value. A_i is given by

$$A_i = 1{,}96\sqrt{\frac{1}{n} + A_{i0}^2} \tag{23}$$

where

1,96 is the 0,975-quantile of the standard normal distribution (see Annex A);

n is the number of measurement results;

A_{i0} is the ratio of standard measurement uncertainty of the accepted reference value to the repeatability standard deviation of the measurement method, A_{i0} is given by

$$A_{i0} = u(\mu)/\sigma_r$$

where $u(\mu)$ is the standard measurement uncertainty of the accepted reference value.

6.4 Requirements of the accepted reference values

The requirements given in 5.4 should be achieved except those

— related to the transportation conditions;

— on the measurement uncertainty limits of the accepted reference value, which should be controlled as low as possible and can be neglected when $u(\mu) < 0{,}3\sigma_r\sqrt{n}$.

If the measurement uncertainty of the accepted reference value is higher than $\sigma_r\sqrt{n}$, e.g. it is hard to obtain a suitable material, the number of measurements should be increased, so that the value of A_i can be reduced to the level that the predetermined absolute value of laboratory bias can be detected with a high probability.

6.5 Carrying out the experiment

6.5.1 Check of the within-laboratory standard deviation

6.5.1.1 Prior to conducting the assessment of laboratory bias, a check of the within-laboratory standard deviation by comparing with the stated repeatability standard deviation of the standard measurement method shall be performed.

6.5.1.2 Compute the average, $\bar{y}_i$, of the n measurement results and s_i, the estimate of the within-laboratory standard deviation, σ_i, as follows:

$$\bar{y}_i = \frac{1}{n}\sum_{k=1}^{n} y_{ik} \tag{24}$$

where

$\bar{y}_i$ is the average of the n measurement results;

n is the number of measurement results;

y_{ik} is the k^{th} independent measurement result.

$$s_i = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(y_k - \bar{y}_i)^2} \tag{25}$$

where s_i is the estimate of the within-laboratory standard deviation.

6.5.1.3 The measurement results shall be scrutinized for outliers using relevant statistical techniques, such as Grubbs' test, as described in ISO 5725-2.

6.5.1.4 If the repeatability standard deviation, σ_r, of the standard measurement method has been established, the estimate s_i can be assessed by the following procedure:

Compute the ratio

$$C'' = (s_i / \sigma_r)^2 \tag{26}$$

and compare the value C" with the critical value

$$C''_{\text{crit}} = \chi^2_{(1-\alpha)}(\nu)/\nu$$

where $\chi^2_{(1-\alpha)}(\nu)$ is the $(1 - \alpha)$-quantile of the χ^2 distribution with $\nu = n - 1$ degrees of freedom.

a) $C'' \leq C''_{\text{crit}}$: s_i is not significantly larger than σ_r.

b) $C'' > C''_{\text{crit}}$: s_i is significantly larger than σ_r.

In the former case, the repeatability standard deviation of the measurement method, σ_r, is to be used for the assessment of the laboratory bias.

In the latter case, consideration should be given to repeating the experiment with verification at all steps that the standard measurement method is properly implemented.

6.5.2 Estimation of the laboratory bias

6.5.2.1 The estimate, $\hat{\Delta}$, of the laboratory bias Δ is given by

$$\hat{\Delta} = \bar{y}_i - \mu \tag{27}$$

6.5.2.2 The measurement uncertainty of the estimate of the laboratory bias is due to the variation in the results of the measurement process and the variation of the accepted reference value. In the case of a known repeatability standard deviation, it is expressed by its standard deviation computed as

$$\sigma_{\hat{\Delta}} = \sqrt{\frac{\sigma_r^2}{n} + u^2(\mu)} \tag{28}$$

or, in the case of an unknown repeatability standard deviation, as

$$s_{\hat{\Delta}} = \sqrt{\frac{s_i^2}{n} + u^2(\mu)} \tag{29}$$

6.5.2.3 The 0,95 confidence interval of the laboratory bias can be computed as

$$\left[\hat{\Delta}-A_i\sigma_r\,,\ \hat{\Delta}+A_i\sigma_r\right] \tag{30}$$

where A_i is as given in Formula (23). If σ_r is unknown, its estimate, s_r, shall be used instead.

6.5.2.4 If this confidence interval contains the value zero, the laboratory bias is insignificant at the significance level α = 0,05; otherwise it is significant.

NOTE The laboratory bias is further considered in ISO 5725-6.

7 Report to the panel and decisions to be taken by the panel

7.1 Cross-reference to ISO 5725-2

The personnel and their duties involved in the experiment shall refer to those described in ISO 5725-2.

7.2 Report by the statistical expert

Having completed the statistical analysis, the statistical expert shall write a report to be submitted to the panel. In this report, the following information shall be given:

a) a full account of the observations received from the operators and/or supervisors concerning the standard measurement method;

b) a full account of the laboratories that have been rejected as outlying laboratories, together with the reasons for their rejection;

c) a full account of any stragglers and/or outliers that have been identified, and whether these were explained and corrected, or discarded;

d) a table of the final estimates of appropriate means and precision measures;

e) a statement on whether the bias of the standard measurement method with respect to the accepted reference used is significant; if so, the estimated value of the bias for each level of property shall be reported.

7.3 Decisions by the panel

The panel should then discuss the statistical expert's report and take decisions concerning the following questions.

a) Are the discordant measurement results, if any, due to defects in the description of the measurement method?

b) What action should be taken with respect to rejected outlying laboratories?

c) Do the results of outlying laboratories and/or the comments received from the operators and supervisors indicate a need to improve the standard measurement method? If so, what are the improvements required?

d) Do the results of the accuracy experiment justify the acceptability of the measurement method for adoption as a standard? What action is to be taken concerning its publication? (e.g., bias can be estimated as negligible (not statistically significant) at only certain levels of the property. These cases can require the panel to suggest reducing the working range of the measurement method.

Annex A
(informative)

Derivation of formulae

A.1 Formulae (3) and (4)

The minimum number of laboratories, p, and of measurement results, n, are calculated to satisfy the two following conditions:

a) the test should be able to detect that the bias is equal to zero with the probability $1 - \alpha = 0{,}95$;

b) the test should be able to detect a predetermined absolute value of bias, δ_m, with the probability $1 - \beta = 0{,}95$.

The first condition is actually developed in 5.5.3.3, where the confidence interval for the bias of the measurement method, δ, is used to carry out a statistical test of the null hypothesis that the absolute value of bias is equal to zero (H_0:$|\delta| = 0$) against the alternative hypothesis that the absolute value of bias is not equal to zero (H_1:$|\delta| \neq 0$).

An equivalent form of this test is to compare the absolute value of the estimate of the bias of the measurement method

$$\left|\hat{\delta}\right| = \left|\bar{\bar{y}} - \mu\right|$$

with a critical value K, and reject $H_0(|\delta| = 0)$ if $\left|\hat{\delta}\right| > K$ [and not reject $H_0(|\delta| = 0)$ if $\left|\hat{\delta}\right| \leq K$],

K is computed using the requirement that the probability of rejecting H_0, if it is true, shall be equal to the chosen significance level $\alpha = 0{,}05$:

$$P\left(\left|\hat{\delta}\right| > K \,\middle|\, |\delta| = 0\right) = \alpha = 0{,}05$$

$$P\left(\left|\hat{\delta}\right| \leq K \,\middle|\, |\delta| = 0\right) = 1 - \alpha = 0{,}95 = \Phi\left(\frac{K}{\sqrt{V\left(\hat{\delta}\right)}}\right) - \Phi\left(-\frac{K}{\sqrt{V\left(\hat{\delta}\right)}}\right) = 2\Phi\left(\frac{K}{\sqrt{V\left(\hat{\delta}\right)}}\right) - 1$$

$$\Phi\left(\frac{K}{\sqrt{V\left(\hat{\delta}\right)}}\right) = 0{,}975$$

$$\frac{K}{\sqrt{V\left(\hat{\delta}\right)}} = u_{0{,}975} = 1{,}960$$

$$K = 1{,}960\sqrt{V\left(\hat{\delta}\right)} \qquad \text{(A.1)}$$

where

$\Phi(\ )$ is the cumulative distribution function of the standard normal distribution;

u_P is the P-quantile of the standard normal distribution;

$V(\hat{\delta})$ is the variance of the estimate of the bias of the measurement method.

The second condition is that the test should be able to detect the predetermined absolute value of bias, δ_m, with the probability $1 - \beta = 0{,}95$:

$$P\left(\left|\hat{\delta}\right| > K \,|\, |\delta| = \delta_m\right) = 0{,}95$$

$$P\left(\left|\hat{\delta}\right| \le K \,|\, |\delta| = \delta_m\right) = \beta = 0{,}05 = P\left(\frac{\hat{\delta} - \delta_m}{\sqrt{V(\hat{\delta})}} \le \frac{K - \delta_m}{\sqrt{V(\hat{\delta})}}\right) = \Phi\left(\frac{K - \delta_m}{\sqrt{V(\hat{\delta})}}\right)$$

$$\frac{K - \delta_m}{\sqrt{V(\hat{\delta})}} = u_{0{,}05} = -1{,}645$$

$$K = \delta_m - 1{,}645\sqrt{V(\hat{\delta})} \tag{A.2}$$

Equating the two expressions (Formulae A.1 and A.2) for K gives

$$1{,}960\sqrt{V(\hat{\delta})} = \delta_m - 1{,}645\sqrt{V(\hat{\delta})}$$

$$(1{,}960 + 1{,}645)\sqrt{V(\hat{\delta})} = \delta_m$$

$$\left(1 + \frac{1{,}645}{1{,}960}\right) 1{,}960\sqrt{V(\hat{\delta})} = \delta_m$$

$$1{,}84 A\sigma_R = \delta_m \tag{A.3}$$

The variance of the estimate of the bias of the measurement method, $V(\hat{\delta})$, can be derived as follows,

$$V(\hat{\delta}) = V(\bar{\bar{y}} - \mu) = V(\bar{\bar{y}}) + u^2(\mu) \tag{A.4}$$

where

$u(\mu)$ is the standard measurement uncertainty of the accepted reference value obtained from an independent study;

$V(\bar{\bar{y}})$ is the variation of the grand mean obtained from this experiment,

$$V(\bar{\bar{y}})=\frac{\sigma_L^2}{p}+\frac{\sigma_r^2}{pn}=\frac{\sigma_R^2-\sigma_L^2}{p}+\frac{\sigma_r^2}{pn}=\frac{n\left(\sigma_R^2-\sigma_R^2/\gamma^2\right)+\sigma_R^2/\gamma^2}{pn}=\left(\frac{n\left(\gamma^2-1\right)+1}{\gamma^2 pn}\right)\sigma_R^2$$

σ_L^2 is the between-laboratory variance so that

$\sigma_R^2=\sigma_L^2+\sigma_r^2$ and $\gamma = \sigma_R/\sigma_r$

Let $A_0 = u(\mu)/\sigma_R$,

$$A=1{,}96\sqrt{\frac{n\left(\gamma^2-1\right)+1}{\gamma^2 pn}+A_0^2} \tag{A.5}$$

A.2 Formulae (22) and (23)

These formulae follow immediately if in the preceding derivation (A.1) δ, δ_m, $\hat{\delta}$, $V(\hat{\delta})$, A and A_0 are replaced by Δ, Δ_m, $\hat{\Delta}$, $V(\hat{\Delta})$, A_i and A_{i0}, respectively, and the expression for $V(\hat{\delta})$ is replaced by the expression

$$V(\hat{\Delta})=\frac{\sigma_r^2}{n}+u^2(\mu)$$

Annex B
(informative)

Example of an accuracy experiment

B.1 Description of the experiment

An accuracy experiment on the determination of manganese content in iron ores by an X-ray fluorescence spectrometry method and using five materials with the accepted reference values (μ) is given in Table B.1 (which were not disclosed to the laboratories). Each laboratory received two, randomly selected, bags of sample for each level of manganese content and performed (under repeatability conditions) duplicate analyses on each bag. The purpose of the two-bag system was to confirm absence of the between-bag variation. The analysis was performed such that in the case where absence of between-bag variation is confirmed, the four analytical results can be considered as replicates under repeatability conditions. Analysis of the results showed that the between-bag variation was indeed insignificant; the materials were regarded to be homogeneous. Thus, results from each laboratory can be considered as replicates under repeatability conditions. The analytical results are listed in Table B.2. The laboratory means and variances for each of the five materials are listed in Table B.3.

B.2 Precision assessment

To assess the precision of the analytical method, the data were analysed by the procedure described in ISO 5725-2. The measurement results for concentration level 1, 2, 3, 4 and 5 of manganese content are shown in Figure B.1, Figure B.2, Figure B.3, Figure B.4 and Figure B.5.

The stragglers and outliers for both Cochran's and Grubbs' tests were identified and are listed in Table B.4. The boxed points in Figures B.1 to B.5 signify that the measurement results were identified as stragglers or outliers. Table B.4 shows that two sets of results from two laboratories (Lab. 3 and 7) at two levels of manganese content were identified as outliers by Cochran's test; and one set of results from one laboratory (Lab. 1) at one level of manganese content was identified as stragglers by Grubbs' test.

The Mandel's h and Mandel's k values are shown in Figures B.6 and Figure B.7. The Mandel's h values (Figure B.6) show clearly that laboratory 1 gets somewhat lower results at level 2, and they were also identified by Grubbs' test as stragglers. The Mandel's k values (Figure B.7) show that laboratories 3 and 7 tend to get much larger within-laboratory variation than the others respectively at the content level 1 and level 5. Appropriate action should be taken by investigating these laboratories, or, if necessary, by tightening the protocol of the measurement method.

For the analysis, it was decided to discard the outliers identified by Cochran's test; i.e. the data at content levels 1 of laboratory 3 and the data at content level 5 of laboratory 7.

The repeatability and the reproducibility standard deviations were then computed excluding those data that were identified. The results of this computation are summarized in Table B.5 and plotted against the level in Figure B.8. Figure B.8 shows that a linear function seems to be an appropriate relationship between the precisions (repeatability standard deviation, s_r, or reproducibility standard deviation, s_R) and content levels, m. The linear regression formulae of the repeatability and reproducibility standard deviations versus content levels are:

$$s_r = 0{,}009\ 25m + 0{,}001\ 15$$

$$s_R = 0{,}018\ 81m + 0{,}002\ 02$$

B.3 Trueness assessment

The trueness of the measurement method was assessed by computing the 0,95 confidence intervals of the bias of the measurement method using Formula (19) and comparing them with zero (Table B.5). Since at all content levels these confidence intervals contain the value zero, the bias of this measurement method is insignificant at the significance level $\alpha = 0{,}05$.

B.4 Further analysis

Further information can be extracted from the data by carrying out supplementary analyses such as a regression analysis of $\bar{\bar{y}}$ versus μ.

Table B.1 — Manganese content in iron ores: accepted reference values

Content level	1	2	3	4	5
Accepted reference value μ (%)	0,028 0	0,127	0,403	0,650	0,80
Expanded measurement uncertainty, U_{95}(%)	0,001 4	0,003 9	0,006 6	0,009 2	0,01
Standard measurement uncertainty, $u(\mu)$ (%)	0,000 7	0,002 0	0,003 3	0,004 6	0,005 0

Table B.2 — Manganese content in iron ores: analytical results as percentage Mn

Unit: %

Lab. No.	Bottle No.	Content level									
		1		2		3		4		5	
1	1	0,024 9	0,025 9	0,118 1	0,118 5	0,412 7	0,415 0	0,689 8	0,682 6	0,821 4	0,818 9
	2	0,024 9	0,024 6	0,117 7	0,117 8	0,413 9	0,415 5	0,683 9	0,690 3	0,828 3	0,824 9
2	1	0,031 6	0,031 3	0,135 2	0,135 0	0,397 5	0,401 5	0,660 3	0,666 5	0,782 0	0,787 6
	2	0,030 8	0,031 5	0,135 4	0,135 4	0,402 4	0,400 9	0,649 4	0,656 6	0,788 7	0,786 7
3	1	0,022 2	0,022 4	0,130 5	0,130 2	0,400 6	0,400 4	0,659 8	0,660 4	0,791 0	0,790 8
	2	0,027 1	0,027 3	0,130 3	0,130 1	0,400 1	0,400 3	0,659 7	0,660 3	0,790 5	0,790 9
4	1	0,027 1	0,029 0	0,128 3	0,127 7	0,408 7	0,407 2	0,660 3	0,669 2	0,804 6	0,802 2
	2	0,028 8	0,027 6	0,129 8	0,128 2	0,404 2	0,408 5	0,663 2	0,663 2	0,801 9	0,802 8
5	1	0,027 1	0,027 1	0,128 6	0,128 6	0,395 7	0,396 5	0,659 8	0,661 3	0,783 0	0,781 4
	2	0,027 1	0,027 1	0,129 3	0,129 3	0,395 7	0,395 7	0,654 4	0,655 2	0,782 2	0,783 0
6	1	0,024 4	0,026 7	0,127 9	0,130 3	0,405 4	0,404 3	0,660 3	0,660 3	0,795 4	0,787 2
	2	0,025 1	0,025 2	0,127 9	0,128 4	0,406 7	0,403 0	0,661 7	0,660 8	0,791 6	0,794 1
7	1	0,026 9	0,028 3	0,128 8	0,126 2	0,387 8	0,383 3	0,641 8	0,634 1	0,830 2	0,799 4
	2	0,027 0	0,026 0	0,124 3	0,128 4	0,388 7	0,380 1	0,637 2	0,635 4	0,800 8	0,831 5
8	1	0,027 2	0,026 3	0,127 1	0,129 5	0,390 0	0,401 6	0,642 0	0,641 6	0,825 0	0,831 9
	2	0,027 9	0,026 5	0,124 2	0,128 6	0,395 5	0,391 5	0,635 2	0,632 5	0,815 1	0,829 2
9	1	0,026 8	0,027 2	0,129 8	0,130 1	0,400 4	0,405 4	0,668 5	0,674 9	0,789 0	0,790 3
	2	0,027 4	0,027 5	0,129 7	0,130 2	0,400 4	0,403 0	0,661 7	0,651 7	0,785 9	0,788 4
10	1	0,029 3	0,030 4	0,133 8	0,131 2	0,404 4	0,404 7	0,659 1	0,662 0	0,790 3	0,786 8
	2	0,029 2	0,030 1	0,133 7	0,130 8	0,400 1	0,408 1	0,649 1	0,653 8	0,790 3	0,786 9
11	1	0,031 1	0,030 6	0,133 6	0,135 5	0,408 1	0,408 4	0,677 0	0,662 8	0,796 2	0,796 9
	2	0,030 4	0,029 4	0,135 2	0,135 9	0,407 4	0,406 8	0,676 5	0,670 1	0,790 6	0,803 8
12	1	0,025 9	0,026 3	0,132 5	0,127 7	0,410 0	0,412 7	0,639 7	0,640 3	0,798 5	0,803 7
	2	0,025 0	0,025 7	0,129 7	0,130 9	0,400 3	0,407 7	0,641 3	0,641 8	0,815 6	0,812 7

Table B.3 — Manganese content in iron ores: laboratory means and laboratory variances

Lab. No.	Content level 1	2	3	4	5
Laboratory mean (Unit: %)					
1	0,025 1	0,118 0	0,414 3	0,686 7	0,823 4
2	0,031 3	0,135 3	0,400 6	0,658 2	0,786 3
3	0,024 8	0,130 3	0,400 4	0,660 1	0,790 8
4	0,028 1	0,128 5	0,407 2	0,664 0	0,802 9
5	0,027 1	0,129 0	0,395 9	0,657 7	0,782 4
6	0,025 4	0,128 6	0,404 9	0,660 8	0,792 1
7	0,027 1	0,126 9	0,385 0	0,637 1	0,815 5
8	0,027 0	0,127 4	0,394 7	0,637 8	0,825 3
9	0,027 2	0,130 0	0,402 3	0,664 2	0,788 4
10	0,029 8	0,132 4	0,404 3	0,656 0	0,788 6
11	0,030 4	0,135 1	0,407 7	0,671 6	0,796 9
12	0,025 7	0,130 2	0,407 7	0,640 8	0,807 6
Laboratory variance [Unit: $(\%)^2$]					
1	$3{,}23 \times 10^{-7}$	$1{,}29 \times 10^{-7}$	$1{,}55 \times 10^{-6}$	$1{,}57 \times 10^{-5}$	$1{,}68 \times 10^{-5}$
2	$1{,}27 \times 10^{-7}$	$3{,}67 \times 10^{-8}$	$4{,}58 \times 10^{-6}$	$5{,}11 \times 10^{-5}$	$8{,}70 \times 10^{-6}$
3	$8{,}02 \times 10^{-6}$	$2{,}92 \times 10^{-8}$	$4{,}33 \times 10^{-8}$	$1{,}23 \times 10^{-7}$	$4{,}67 \times 10^{-8}$
4	$8{,}49 \times 10^{-7}$	$8{,}20 \times 10^{-7}$	$4{,}31 \times 10^{-6}$	$1{,}40 \times 10^{-5}$	$1{,}46 \times 10^{-6}$
5	0	$1{,}63 \times 10^{-7}$	$1{,}60 \times 10^{-7}$	$1{,}15 \times 10^{-5}$	$5{,}87 \times 10^{-7}$
6	$9{,}37 \times 10^{-7}$	$1{,}30 \times 10^{-6}$	$2{,}48 \times 10^{-6}$	$4{,}36 \times 10^{-7}$	$1{,}30 \times 10^{-5}$
7	$8{,}97 \times 10^{-7}$	$4{,}37 \times 10^{-6}$	$1{,}61 \times 10^{-5}$	$1{,}13 \times 10^{-5}$	$3{,}16 \times 10^{-4}$
8	$5{,}29 \times 10^{-7}$	$5{,}39 \times 10^{-6}$	$2{,}69 \times 10^{-5}$	$2{,}23 \times 10^{-5}$	$5{,}43 \times 10^{-5}$
9	$9{,}58 \times 10^{-8}$	$5{,}67 \times 10^{-8}$	$5{,}77 \times 10^{-6}$	$9{,}85 \times 10^{-5}$	$3{,}41 \times 10^{-6}$
10	$3{,}50 \times 10^{-7}$	$2{,}55 \times 10^{-6}$	$1{,}07 \times 10^{-5}$	$3{,}27 \times 10^{-5}$	$3{,}97 \times 10^{-6}$
11	$5{,}09 \times 10^{-7}$	$1{,}02 \times 10^{-6}$	$5{,}16 \times 10^{-7}$	$4{,}43 \times 10^{-5}$	$2{,}93 \times 10^{-5}$
12	$2{,}96 \times 10^{-7}$	$4{,}09 \times 10^{-6}$	$2{,}83 \times 10^{-5}$	$9{,}02 \times 10^{-7}$	$6{,}27 \times 10^{-5}$

Table B.4 — Manganese content in iron ores: outliers and stragglers

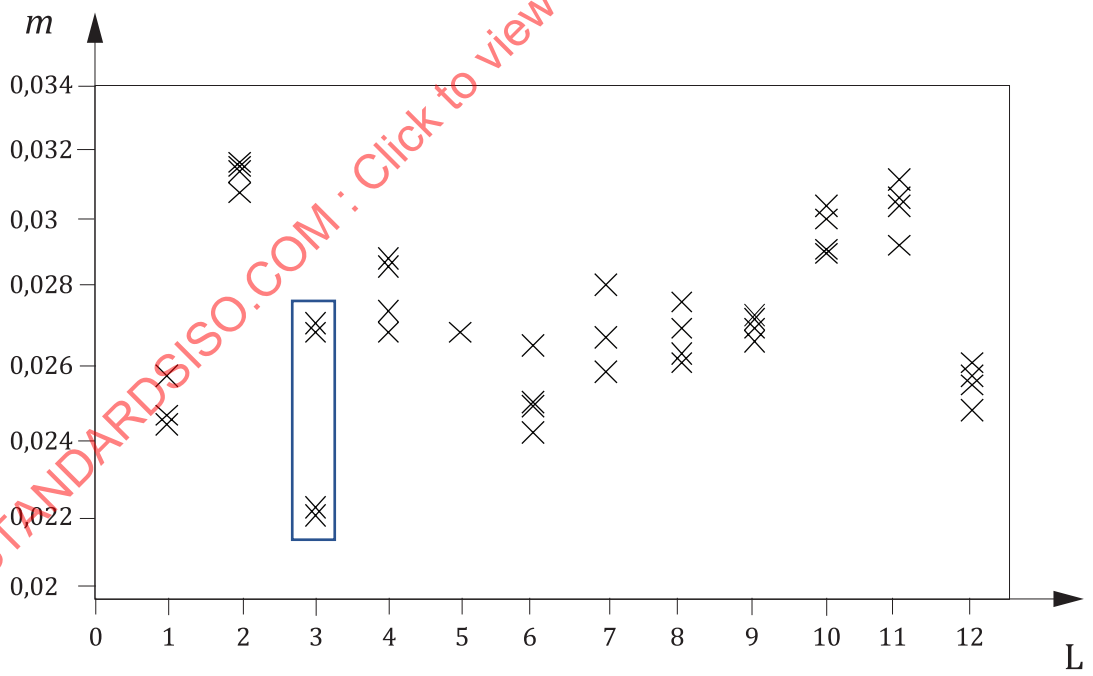
Content level	Lab	Calculated statistic[a]	Critical value[a]
List of outliers ($\alpha = 0{,}01$)			
1	3	$C = 0{,}620$	$C_{0,01}(4,12) = 0{,}392$
5	7	$C = 0{,}619$	$C_{0,01}(4,12) = 0{,}392$
List of stragglers ($\alpha = 0{,}05$)			
2	1	$G1 = 2{,}531$	$G1_{0,05}(12) = 2{,}412$, $G1_{0,01}(12) = 2{,}636$
[a] C=Cochran's test; $G1$=Grubbs' test for one smallest outlying observation.			

Table B.5 — Manganese content in iron ores: estimation of repeatability and reproducibility standard deviations and bias of the measurement method

	Content level 1	2	3	4	5
n	4	4	4	4	4
p	11	12	12	12	11

Table B.5 *(continued)*

	Content level				
	1	2	3	4	5
$\bar{\bar{y}}$, %	0,027 6	0,129 3	0,402 1	0,657 9	0,798 6
s_r, %	0,001 16	0,002 23	0,005 04	0,008 70	0,007 28
s_R, %	0,002 29	0,004 85	0,008 79	0,016 12	0,015 97
γ	1,98	2,17	1,75	1,85	2,19
A_y	0,271 0	0,264 8	0,250 6	0,255 2	0,277 0
$A_y s_R$, %	0,000 62	0,001 28	0,002 20	0,004 12	0,004 42
$0{,}3A_y$	0,081 3	0,079 4	0,075 2	0,076 6	0,083 1
$0{,}3A_y s_R$, %	0,000 19	0,000 39	0,000 66	0,001 23	0,001 33
μ,%	0,028	0,127	0,403	0,650	0,80
u(μ), %	0,000 7	0,002 0	0,003 3	0,004 6	0,005 0
A_0	0,305 9	0,401 8	0,375 3	0,285 3	0,313 1
A	0,801 1	0,943 2	0,884 6	0,750 2	0,819 4
As_R, %	0,001 83	0,004 58	0,007 78	0,012 10	0,013 08
$\hat{\delta}$, %	-0,000 4	0,002 3	-0,000 9	0,007 9	-0,001 4
$\hat{\delta} - As_R$, %	-0,002 2	-0,002 3	-0,008 7	-0,004 2	-0,014 5
$\hat{\delta} + As_R$, %	0,001 5	0,006 9	0,006 8	0,020 0	0,011 7



Key

m manganese content in percent

L laboratory No.

NOTE Boxed points signify that the measurement results were identified as outliers by Cochran's test.

Figure B.1 — Manganese content in iron ores — Measurement results at content level 1