TECHNICAL REPORT

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# Paints and varnishes — Guidelines for the determination of the precision of a test method by interlaboratory trials

*Peintures et vernis — Lignes directrices pour la détermination de la fidélité d'une méthode d'essai par essais interlaboratoires*

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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# 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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.

ISO/TR 24430 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

# Introduction

These guidelines contain recommendations on the conduct of interlaboratory trials, so called “round robins”, to determine the precision to be expected when undertaking tests on paints, varnishes and related materials and the coatings derived from them. It is not designed to give a full treatment of the subject but, rather, to indicate the important features of the process and, where appropriate, to refer to other publications which give fuller details of the matters under discussion.

The accepted meaning of precision as discussed in this document is the closeness of agreement between test results. It does not relate to the true value or an accepted reference value.

The need to consider precision arises because tests performed on identical materials in identical conditions do not, usually, yield identical results. This is attributed to unavoidable random errors inherent in every test procedure. Knowledge of the extent to which these random errors influence the test results is an important aspect of determining the validity of such results.

# Paints and varnishes — Guidelines for the determination of the precision of a test method by interlaboratory trials

## 1 Scope

The purpose of these guidelines is:

— to give recommendations on how to introduce precision statements into an International Standard which specifies a test method for paints, varnishes, related materials and coatings derived from them;

— to outline the general principles to be applied when assessing precision in order to establish the procedures which will enable a quantitative estimate to be made;

— to outline the general principles under which interlaboratory trials should be conducted.

These guidelines may be applied to paints, varnishes and related products, to their raw materials in solid, liquid or powder form and to coatings derived from them.

The guidelines are concerned only with test methods which operate on a continuous scale to yield a single numerical figure as the test result. However, this single figure may be the outcome of a calculation from a set of measurements. The distribution of test results is required to be unimodal and is assumed to be normal. With non-Gaussian distributions other evaluation procedures will be necessary. It does not cover methods which yield discrete values such as go no-go tests or where a ranking scheme is in operation.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3534-1, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms*

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 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

ASTM E691, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method*

## 3 Terms and definitions

For the purposes of this document the terms and definitions given in ISO 3534-1 and the following apply.

**3.1**
**observed value**
the value of a property obtained as a result of a single observation

**3.2**
**test result**
the value of a property obtained by carrying out a specified test method

NOTE The test method should specify that one or a number of individual observations be made and their average or another appropriate function (such as the median or the standard deviation) be reported as the test result. It may also require standard corrections to be applied, such as for gas volumes to standard temperature and pressure. Thus, a test result can be calculated from several observed values. In the simplest case, the test result is the observed result itself.

**3.3**
**test level**
the general average of the test results from all laboratories for one particular material or specimen tested

**3.4**
**cell**
the test results at a single level obtained by one laboratory

**3.5**
**precision**
the closeness of agreement between test results obtained under stipulated conditions such that they are not influenced by any previous result on the same or similar material

NOTE The measure of precision is usually expressed as, or derived from, a standard deviation, which is a measure of imprecision as computed from the test data. Less precision is reflected by a larger standard deviation.

**3.6**
**repeatability**
a measure of the dispersion of test results under conditions where test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time

**3.7**
**reproducibility**
a measure of the dispersion of test results under conditions where test results are obtained with the same method on the same test material in different laboratories with different operators using different equipment

**3.8**
**outlier**
a member of a set of values, which is inconsistent with the other members of that set

**3.9**
**degrees of freedom**
the number of independent observations

NOTE Where only one parameter is under study (as is assumed in these guidelines) the number of degrees of freedom will be N −1 where N is the number of samples.

# 4 Requirements for an interlaboratory precision experiment

A collaborative interlaboratory trial is made to get test results which are needed to compute the precision of a test method. A flow chart for the process is given in Annex A. See also ASTM E691.

## 4.1 General

The information in this document is intended to give an outline of the requirements. For any particular application the information needs to be completed by additional information, which should be agreed by the participants in the trial. See ASTM E691.

For a successful experiment it is essential that:

— the participating laboratories and personnel are given all the details before the start of the exercise;

— all participating laboratories keep to the instructions for carrying out the experiment;

— all operators are familiar with the test method;

— all measurements taken are reported;

— no more than the number of replicates specified are carried out;

— the mean of a series of replicates is not reported as a single observed value.

## 4.2 Personnel requirements

### 4.2.1 The executive officer/project manager

The executive officer takes full responsibility for the organisation of the experiment and supervises its execution. He should be familiar with the test method and should consult the convenor of the participating working group on the ranges and levels needed for the entire field of application. He designs the experiment, collects the test results and determines the numerical value of the precision.

### 4.2.2 The statistician

Ideally, the executive officer or an assistant operator should have good experience in the statistical design and analysis of experiments. Otherwise, assistance of a person familiar with the necessary statistical procedures should be obtained.

### 4.2.3 The operator

In each of the participating laboratories the experiment must be performed by an operator who is representative of the type of person who usually carries out this sort of measurement.

## 4.3 Instructions for the interlaboratory trial

### 4.3.1 Test method

The operator shall be given clear and full instructions about the test procedure.

NOTE It is very important that all measurements are made at around the same time as the properties of a sample can change with time.

#### 4.3.2 Measurement range

The interlaboratory experiment must cover the entire measurement range by samples and/or substrates representing the different levels of the test. The quantity of material prepared should be sufficient for the trial and allow an adequate stock in reserve.

#### 4.3.3 Sampling and transport

To eliminate all variables in the preparation of test samples, this operation should be centralised to ensure that an identical product is supplied to all operators. The samples should be transported to the participating laboratories under specified controlled conditions.

#### 4.3.4 Number and labelling of samples

The number of samples to be tested, the number of repeat measurements and the order in which these are to be undertaken is to be specified. Samples shall be allocated and distributed from one place, preferably by the executive officer or by one of the operators. Prepare from each material enough samples to provide the test material for the participating laboratories and a sufficient number of additional samples for replacement of lost or spoiled samples. For this purpose it is recommended that each sample be labelled with a three or five digit random number. Each laboratory should test in order of increasing sample number. The allocation of random numbers should be known only to the executive officer.

#### 4.3.5 Number of observations to be made

The number of observations to be made must be specified for each sample and laboratory. Measurements for repeatable conditions must be undertaken by the same operator using the same apparatus.

#### 4.3.6 Timing of the experiment

If necessary, a precise time shall be specified when the measurements shall be carried out. The date of the test must be reported. It may be necessary to specify how the samples are to be conditioned prior to the test.

#### 4.3.7 Test report

A special form is recommended for this purpose, which is to be supplied with the samples. The form should show the sample numbers and the required data with the units of measurement and the number of significant places. Spaces for the observed values and the test results should be included together with the date of the experiment and the name of the operator. Room for recording observations and anomalies by the operator should be available. The form should also include the name and address of the experimental officer to whom it should be sent.

#### 4.3.8 Comments

The operator should report any anomaly or difficulty experienced and any inadequacies in the instructions or the test method.

### 4.4 Minimum conditions for interlaboratory experiments

#### 4.4.1 Participating laboratories

The laboratories participating in the experiment to estimate precision should have been chosen at random from all the laboratories using the measurement method. They should not consist exclusively of those that have gained special experience during the process of standardising the method. In the evaluation of a test method, an absolute minimum of three laboratories, or test locations, shall be used, but at least five are strongly recommended.

#### 4.4.2 The number and distribution of samples

The number of samples required to determine a particular statistic shall never be fewer than thirty and, preferably, shall be sixty or more. Samples shall be distributed equally between participating laboratories so that the number of test results on each material in each laboratory is preferably between three and five. It is desirable that samples are examined by more laboratories than that a few laboratories undertake a large number of tests.

## 5 Conducting the test

### 5.1 Programme

The statistician shall examine the programme to check its suitability for purpose.

### 5.2 Pilot run

Before undertaking the full study it may be advisable to conduct a pilot run to familiarise the operators with the procedures and to ensure they are properly understood. The results of the pilot study shall be evaluated by the project manager before commencing the main programme.

### 5.3 Progress monitoring

The project manager shall check on a regular basis that testing in each laboratory is being undertaken at a satisfactory pace.

### 5.4 Replacement samples

The project manager shall decide on the desirability of supplying further samples in the event of misuse of the originals.

### 5.5 Inspection of data

The project manager shall receive from each laboratory the completed results immediately following the completion of the tests for examination to determine whether further action, such as the supply of replacement samples, is required.

## 6 Computing the precision — The statistical analysis

See ISO 5725-2.

NOTE 1 This clause illustrates only those cases where the simplest (normal) type of distribution is encountered. It is essential that a person with sufficient experience is employed so that non-Gaussian distributions are recognised and properly handled.

NOTE 2 It is to be expected that the calculations will be undertaken using a suitable computer programme package. Ensure that the programme retains at least two extra digits in the calculations to ensure statistically important information is not lost.

The relevant equations to be used in the calculations are:

i) Average $\bar{X} = \sum X / N$

ii) Standard deviation $S = \sqrt{\sum \left( X - \bar{X} \right)^2 / \left( N - 1 \right)}$

where

$X$ are the individual test results.

$\bar{X}$ is the calculated average.

$N$ is the number of items.

$S$ is the calculated standard deviation.

## 6.1 Data correction

### 6.1.1 Redundant data

Sometimes a laboratory will report more test results than those officially required. The project manager will have to decide which should be rejected either on the basis of knowledge or by random selection.

### 6.1.2 Missing data

Unless these are so excessive as to hazard the validity of the study, they should be ignored in the analysis apart from necessary procedural adjustments.

### 6.1.3 Outliers

Experience has taught that outliers cannot be avoided and have to be taken into consideration. As a general rule no readings should be rejected unless either, there is evidence for a definite source of error or, they fail some statistical criteria. It should be noted that not only individual results but data from a source (i.e. a laboratory) may be subject to this procedure. Under no circumstances, after rejection of outliers, may a further analysis be undertaken to detect further outliers inconsistent with the adjusted data set. For an extensive treatment on the subject see ISO 5725-2 or ASTM E691.

## 6.2 Dependence of precision on level

See ISO 5725-2:1994, 7.5.

When the standard deviations for both repeatability and reproducibility do not show any dependence on the level of test it is permissible to average the values before calculation of the precision. Otherwise, following suitable statistical tests to check for homogeneity (see ISO 5725-2:1994, 7.3.3, Cochran's test), separate precision values may need to be assigned to each level.

## 6.3 Calculation of precision

See ISO 5725-6:1994, 4.1.2.

The multiplier 2,8 is used to convert the standard deviations to precision values. This represents a 95 % (i.e. 19 in 20) probability that two test results will lie within these limits.

# 7 Reporting precision values

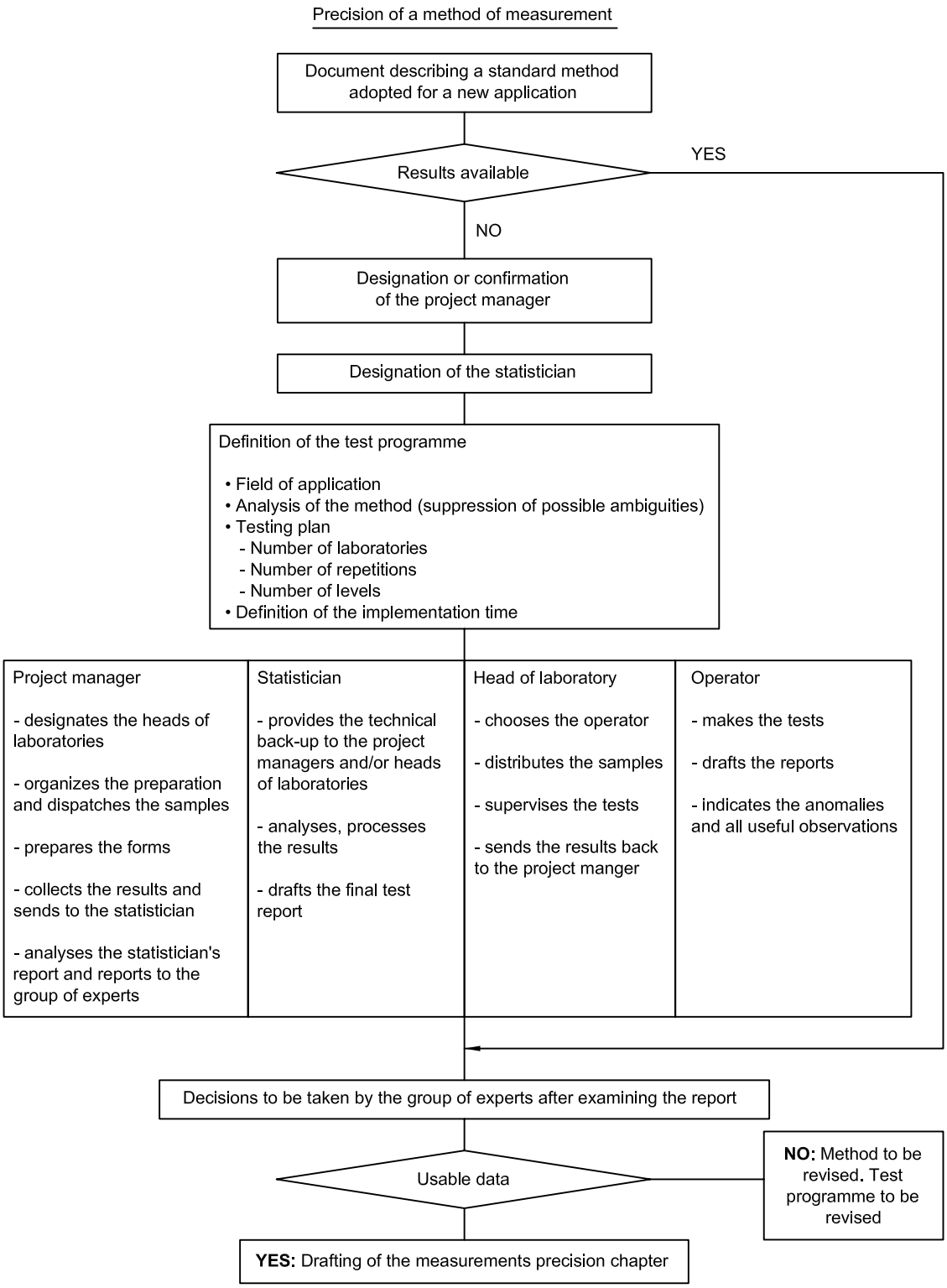
The determined values for repeatability limit ($r$) and reproducibility limit ($R$) are:

$r$ =

$R$ =

The range to which these values are applicable should be stated.

# Annex A
# Description of the process



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