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**Petroleum and related products —  
Precision of measurement methods  
and results —**

**Part 1:  
Determination of precision data in  
relation to methods of test**

*Produits pétroliers — Fidélité des méthodes de mesure et des  
résultats —*

*Partie 1: Détermination des valeurs de fidélité relatives aux  
méthodes d'essai*

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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.

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](http://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](http://www.iso.org/patents)).

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For an explanation on 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 the following URL: [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*.

This first edition of ISO 4259-1, together with ISO 4259-2, cancels and replaces ISO 4259, which has been technically revised.

A list of all parts in the ISO 4259 series can be found on the ISO website.

## Introduction

For purposes of quality control and to check compliance with specifications, the properties of commercial petroleum products are assessed by standard laboratory test methods. Two or more measurements of the same property of a specific sample by a specific test method, or, by different test methods that purport to measure the same property, will not usually give exactly the same result. It is, therefore, necessary to take proper account of this fact, by arriving at statistically based estimates of the precision for a method, i.e. an objective measure of the degree of agreement expected between two or more results obtained in specified circumstances.

This document makes reference to ISO 3534-2<sup>[1]</sup>, which gives a different definition of true value (see 3.23). This document also refers to ISO 5725-2. The latter is required in particular and unusual circumstances (see 5.3.1) for the purpose of estimating precision.

The two parts of ISO 4259 encompass both the derivation of precision estimates and the application of precision data. They combine the information in ASTM D6300<sup>[2]</sup> regarding the determination of the precision estimates and the information in ASTM D3244<sup>[3]</sup> for the utilization of test data.

A glossary of the variables used in this document and ISO 4259-2 is included as [Annex I](#) in this document.

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# Petroleum and related products — Precision of measurement methods and results —

Part 1:

## Determination of precision data in relation to methods of test

### 1 Scope

This document specifies the methodology for the design of an Interlaboratory Study (ILS) and calculation of precision estimates of a test method specified by the study. In particular, it defines the relevant statistical terms (Clause 3), the procedures to be adopted in the planning of ILS to determine the precision of a test method (Clause 4), and the method of calculating the precision from the results of such a study (Clauses 5 and 6).

The procedures in this document have been designed specifically for petroleum and petroleum related products, which are normally considered as homogeneous. However, the procedures described in this document can also be applied to other types of homogeneous products. Careful investigations are necessary before applying this document to products for which the assumption of homogeneity can be questioned.

### 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 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*

### 3 Terms and definitions

For the purposes of this document, the following terms and definitions 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/>

#### 3.1

##### analysis of variance

###### ANOVA

technique that enables the total variance of a method to be broken down into its component factors

#### 3.2

##### accepted reference value

###### ARV

agreed-upon reference value for a specific property of a material determined using an accepted reference method and protocol, e.g. derived from an ILS

**3.3**  
**between laboratory variance**

component of the total variance attributable to the difference between the means of different laboratories

Note 1 to entry: When results obtained by more than one laboratory are compared, the scatter is usually wider than when the same number of tests is carried out by a single laboratory, and there is some variation between means obtained by different laboratories. These give rise to the between laboratory variance which is that component of the overall variance due to the difference in the means obtained by different laboratories.

Note 2 to entry: There is a corresponding definition for between operator variance.

Note 3 to entry: The term “between laboratory” is often shortened to “laboratory” when used to qualify representative parameters of the dispersion of the population of results, for example as “laboratory variance”.

**3.4**  
**bias**

<of a test method> difference between the population mean of test results from a very large number of different laboratories for the property of a material obtained using a specific test method versus the accepted reference value for the property where this is available

Note 1 to entry: See Note 1 to entry in [3.13](#) for an interpretation of “population mean of test results”.

**3.5**  
**blind coding**

assignment of a different number to each sample so that no other identification or information on any sample is given to the operator

**3.6**  
**check sample**

sample taken at the place where a product is exchanged, i.e. where the responsibility for the product quality passes from the supplier to the recipient

**3.7**  
**degrees of freedom**

divisor used in the calculation of variance

Note 1 to entry: The definition applies strictly only in the simplest cases. Definitions for more complex cases are beyond the scope of this document.

**3.8**  
**determination**

process of carrying out the series of operations specified in a test method, whereby a single value is obtained

**3.9**  
**interlaboratory study**  
**ILS**

study specifically designed to estimate the repeatability and reproducibility of a standard test method achieved at a fixed point in time by multiple laboratories through the statistical analysis of their test results obtained on aliquots prepared from multiple materials

**3.10**  
**known value**

quantitative value for a property that can be theoretically derived or calculated by the preparation of the sample

Note 1 to entry: The known value does not always exist, for example for empirical tests such as flash point.

**3.11**  
**mean**

sum of a set of results divided by the number of results

**3.12****mean square**

sum of squares divided by the degrees of freedom

**3.13****normal distribution**

probability distribution of a continuous random variable,  $x$ , such that, if  $x$  is any real number, the probability density is as shown in Formula (1):

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right], -\infty < x < \infty \quad (1)$$

Note 1 to entry: In the context of modelling a distribution of test results,  $\mu$  is the population mean, or true value (see 3.23) of the property as determined by a specific test method;  $\sigma$  is the standard deviation of the normal distribution used to describe the distribution of an infinite number of test results obtained using the same test method by an infinite number of laboratories ( $\sigma > 0$ ).

**3.14****operator**

person who normally and regularly carries out a particular test

**3.15****outlier**

result far enough in magnitude from other results to be considered not a part of the set

**3.16****precision**

closeness of agreement between the results obtained by applying the same test procedure several times on essentially the same materials and under prescribed conditions

Note 1 to entry: The smaller the random part of the experimental error, the more precise the procedure.

**3.17****random error**

component of measurement error that in replicate measurements varies in an unpredictable manner

**3.18****repeatability**

limiting value for the difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, within a short interval of time, under the same test conditions, that is expected to be exceeded with a probability of 5% due to random variation

Note 1 to entry: Same test conditions are to be considered as same operator, same apparatus, same calibration and same laboratory.

Note 2 to entry: The representative parameter for the dispersion of the population that can be associated with these results is repeatability standard deviation or repeatability variance. Repeatability refers to the maximum difference attributable to random variation between two results obtained under the state of minimum random variability. Therefore, the period of time during which repeat results are to be obtained should be short enough to exclude time dependent variation, for example, variation caused by environmental changes, or variation associated with multiple calibrations".

Note 3 to entry: The term "repeatability" is not to be confused with the terms "between repeats" or "repeats".

**3.19  
reproducibility**

limiting value for the difference between two independent results obtained in the normal and correct operation of the same method, for test material considered to be the same, under different test conditions, that is expected to be exceeded with a probability of 5 % due to random variation

Note 1 to entry: Different test conditions are to be considered as different operator, different apparatus, different calibration, and different laboratory.

Note 2 to entry: The representative parameter of the dispersion of the population that can be associated with these results is reproducibility standard deviation or reproducibility variance. Reproducibility refers to the maximum difference attributable to random variation between two results obtained under the state of maximum random variability.

**3.20  
result**

final value obtained by following the complete set of instructions in a test method

Note 1 to entry: It is assumed that the result is rounded off according to the procedure specified in [Annex G](#).

**3.21  
standard deviation**

measure of the dispersion of a series of results around their mean, equal to the positive square root of the variance and estimated by the positive square root of the mean square

**3.22  
sum of squares**

sum of squares of the differences between a series of results and their mean

**3.23  
true value**

for practical purposes, the value towards which the average of single results obtained by  $n$  laboratories tends, as  $n$  tends towards infinity

Note 1 to entry: Such a true value is associated with the particular method of test.

Note 2 to entry: A different and idealized definition is given in ISO 3534-2<sup>1)</sup>.

**3.24  
variance**

mean of the squares of the deviation of a random variable from its mean, estimated by the mean square

## **4 Stages in the planning of an interlaboratory study for the determination of the precision of a test method**

### **4.1 General**

The stages in planning an interlaboratory study (ILS) are as follows:

- a) preparing a draft method of test;
- b) planning a pilot study with at least two laboratories;
- c) planning the ILS;
- d) executing the ILS.

The four stages are described in turn in [4.2](#) to [4.5](#).

## 4.2 Preparing a draft method of test

This shall contain all the necessary details for carrying out the test and reporting the results. Any condition that could alter the results shall be specified.

The ILS shall be designed so that it covers the intended range of the test method (see also 6.5). A clause on precision is included in the draft method of the test at this stage only as a heading.

## 4.3 Planning a pilot study with at least two laboratories

A pilot study is necessary for the following reasons:

- a) to verify the details in the operation of the test;
- b) to find out how well operators can follow the instructions of the method, and thus of the ILS;
- c) to check the precautions regarding samples;
- d) to estimate approximately the precision of the test.

At least two samples are required, covering the range of results to which the test method is intended to apply; however, at least 12 laboratory/sample combinations shall be included. Each sample is tested twice by each laboratory under repeatability conditions. The samples should be equally distributed across the test method range, and should include major product groups covered in the test method scope. If any omissions or inaccuracies in the draft test method are revealed, they shall now be corrected. The results shall be analysed for precision, and bias for sample(s) with accepted reference values. If either is considered to be too large, then alterations to the test method shall be considered.

## 4.4 Planning the ILS

There shall be at least six participating laboratories, but it is recommended this number be increased to eight or more in order to ensure the final precision is based on at least six laboratories and to ensure the precision statement is more representative of the user population.

The number of samples shall be sufficient to adequately represent the types of materials to which the test method is to be applied, to cover the range of the property measured at approximately equidistant intervals, and to give reliability to the precision estimates. If precision is found to vary with the level of results in the pilot study, then at least five samples shall be used in the ILS. In order to correctly estimate precision versus level relationship, it is important that the choice of samples evenly covers the range and materials for the property measured, so that an estimated relationship is not too dependent upon the leverage of a sample with extreme property value.

It is strongly recommended that the leverage of each planned sample in the sample set design,  $lev_i$ , be assessed using [Formula \(2\)](#). No sample shall have a leverage exceeding 0,5. See [Table D.11](#) for an example of leverage calculation (second column from the right under heading ' $lev_i$ ').

$$lev_i = \frac{1}{n} + \frac{(x_i - \bar{x})^2}{\sum_{k=1}^n (x_k - \bar{x})^2} \quad (2)$$

where

$lev_i$  is leverage of sample  $i$ ;

$n$  is total number of planned samples;

$x_i$  is Napierian logarithm,  $\ln(p_i)$ , with  $p_i$  being the planned property level for sample  $i$ ;

$\bar{x}$  is grand average of all  $x_i$ .

In any event, it is necessary to obtain at least 30 degrees of freedom for both repeatability and reproducibility (see [Annex B](#) for the corresponding rationale). For repeatability, this means obtaining a total of at least 30 pairs of results in the ILS.

For reproducibility, [Annex A, Table A.1](#) gives the minimum number of samples required in terms of  $L$ ,  $P$  and  $Q$ , where  $L$  is the number of participating laboratories, and  $P$  and  $Q$  are the ratios of variance component estimates obtained from the pilot study. Specifically,  $P$  is the ratio of the interaction component to the repeats component and  $Q$  is the ratio of the laboratories component to the repeats component. [Annex E](#) gives the derivation of the formula used. If  $Q$  is much larger than  $P$ , then 30 degrees of freedom cannot be achieved; the blank entries in [Table A.1](#) correspond to this situation (i.e. when more than 20 samples are required). For these cases, there is likely to be a significant bias between laboratories.

In the absence of pilot test program information to permit the use of [Table A.1](#), the number of samples shall be greater than five, and chosen such that the number of laboratories times the number of samples is greater than or equal to 42.

When it is known or suspected that different types of materials exhibit different precision functional forms when tested by the test method, consideration should be given to conducting separate ILS for each type of material.

#### 4.5 Executing the ILS

One person shall be responsible for the entire ILS, from the distribution of the texts of the test method and samples to the final appraisal of the results. This person shall be familiar with the test method, but shall not personally take part in the tests.

The text of the test method shall be distributed to all the laboratories in time to allow any queries to be raised before the tests begin. If any laboratory wants to practice the method in advance, than this shall be carried out with samples other than those used in the ILS.

The samples shall be accumulated, subdivided and distributed by the coordinator, who shall also keep a reserve of each sample for emergencies. It is most important that the individual laboratory portions be homogeneous and stable for the property of interest throughout the entire duration of the ILS. Prior to distribution, the ILS sample set shall be blind coded in a manner that preserves the anonymity of the nature of the test material and the expected value of the property. The following information shall be sent with the ILS sample set.

- a) Agreed (draft) method of test.
- b) Handling and storage requirements for the samples.
- c) Order in which the samples are to be tested. A different random order for each laboratory is highly recommended. For large number of laboratories, several unique test orders may be randomly assigned to groups of laboratories, with no more than 4 laboratories per group.
- d) For statistical reasons, it is imperative that the repeat results are obtained independently of each other, i.e. that the second result is not biased by knowledge of the first. This is achieved by blind coding where the repeat for each material in the ILS design is included in the test set sent to ILS participants without disclosing that it is a repeat, with an accompanying statement that a single result is to be obtained on each sample in the test set, in the specified testing order, by the same operator with the same apparatus within a short time. If this blind coding is regarded as infeasible to achieve, then the statement shall state that a pair of results associated with a sample shall be obtained by the same operator with the same apparatus within a short time, without disclosing the nature of the sample.
- e) Period of time within which all the samples are to be tested.

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