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Water quality — Guidance and requirements for designing an interlaboratory trial for validation of analytical methods

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Foreword

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This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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

The final validation step during standardization of an analytical method is the evaluation of performance through an interlaboratory trial to demonstrate that a new method is fit for purpose.

This document is intended to assist persons organizing interlaboratory trials to design and organize international interlaboratory comparisons for the validation of new standardized physical, chemical and biochemical methods for water analysis.

Water quality — Guidance and requirements for designing an interlaboratory trial for validation of analytical methods

1 Scope

This document specifies requirements and recommendations for the design and execution of an interlaboratory comparison for validation of new standardized analytical methods in the field of water analysis, e.g. the number of participating laboratories and time schedules. This document is based on ISO 5725-1 and ISO 5725-2.

NOTE The scope of other standards in the field of interlaboratory comparison, such as ISO/IEC 17043[3] and ISO 13528[1], is proficiency testing of analytical laboratories and not interlaboratory comparison for the validation of analytical methods.

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 5725-1, *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*

3 Terms and definitions

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

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

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

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

4 Principle

A representative number of laboratories analyse within the sample stability period the same sample material prepared and distributed by the organizer of the interlaboratory trial. The results are used to calculate the performance data of the standardized method (see Clause A.3).

5 Preconditions

5.1 General

The prerequisite for the performance of the interlaboratory trial is that the method development and the validation of the individual steps of the whole measurement process according to ISO/TS 13530[2] have been completed.

NOTE 1 Validation of analytical methods is also described in References [4] and [5].

As the aim of this kind of interlaboratory comparison is the evaluation of the performance data of an analytical method, no technical alterations of the given protocol of the standardized analytical method are allowed to the participants of the interlaboratory trial.

NOTE 2 This is in contrast to proficiency testing interlaboratory comparisons, where the participating laboratories use different analytical methods for the determination of the same parameter.

All registered participants of an interlaboratory trial should get all samples. Only in exceptional cases they could be entitled to select samples in advance, because it is important to receive as many test results as possible. It is highly recommended that all samples are tested by the participants and results of all parameters be submitted to the organizer of the interlaboratory trial to ensure a maximum number of individual test results after outlier rejection within the evaluation.

If there are several options within the standardized analytical method, for example, for extraction or detection, separate performance data are evaluated for each option and for the undifferentiated data set. The decision to merge data sets is taken by experts of the interlaboratory trial after examination of the influence of the chosen option on the final measurement result. It is the result of the evaluation of the fitness for purpose of the tested standard.

5.2 Special preconditions for validation of non-crucial method options in analytical methods for organic analytes

This subclause is not applicable to operationally defined analytical methods.

Non-crucial method options mean, only alternatives or variants of single analytical steps, as extraction options or the change to direct injection using a highly developed apparatus instead of a specified enrichment technique are considered non-crucial. But, changing the analytical principle like switching from GC-MS to LC-MS is considered crucial and not the scope of this subclause. The alternatives or options in this sense are not independent methods.

The experts in charge of the development of the standardized analytical method define whether an option is crucial or non-crucial, based on experiments and/or experience.

In general, a method option has to be as well described as a normative method. All necessary references to the method in the main part of the standard and vice versa shall be given. Pre-normative validation work has to be performed as well as for the main method. Results according to the alternatives or options shall be equivalent.

All authorized options of one single analytical step shall be mentioned in the main document. If required, they can be described in detail in an annex. It has to be clear that all the options are equivalent and can be used.

A documented evaluation of any alternative step of a method is needed. This has to be provided by the experts of the responsible working group before carrying out the interlaboratory trial.

The results of the method options/alternatives of the interlaboratory trial are pooled. No separate evaluation of the results of the different options will be performed. The question, which of the options was applied by a laboratory, is merely additional information for documentation of the interlaboratory trial. The experts responsible for the interlaboratory trial have to evaluate the results and document their decision.

6 Design and organization

6.1 Requirements for participation and call for participants

The number of participants has an influence on the reliability of the statistically calculated performance data. A minimum of 24 outlier-free data obtained from a minimum of eight laboratories are mandatory. In this, it is therefore desirable to ensure that the number of laboratories registered for participation in the interlaboratory trial is not less than 12.

Participation in this kind of interlaboratory trials is voluntary. To achieve reliable performance data, only experienced laboratories which are able to analyse all provided test samples applying the analytical procedures described in the corresponding standardized analytical method should participate. Unexperienced laboratories may be excluded from participation. It is the task of the persons responsible of the interlaboratory trial to define, how the laboratory's competence can be demonstrated. The organizer of the interlaboratory trial can demand the analysis of a quality control standard (see 6.2).

Although this goal is not easy to achieve, it is recommended to have global participation and participants from at least five countries. The call for participants for the interlaboratory trial should be distributed not later than five months before the dispatch of the samples. Laboratories should express their interest in participation within four weeks after the announcement of the interlaboratory trial.

If the call for participants yields an insufficient number of laboratories who are experienced with the method, assistance in applying this method should be provided by the responsible organizer of the interlaboratory trial, e.g. by offering interested laboratories familiar with the analytical principle the possibility to participate in a training workshop not later than three months before the dispatch of the samples. Standard solutions for checking calibration and additional information should be provided by the project leader to enable the participants to establish the methods in their laboratories.

NOTE 1 Financing the interlaboratory trial is in the responsibility of the organizer, e.g. by charging his/her institution, fund-raising, or requesting participation fees to compensate for materials and mailing expenses.

NOTE 2 If water samples are to be shipped to a foreign country, difficulties with export regulations can occur and have to be checked in advance.

6.2 Samples

In general, real or spiked real samples shall be given preference over synthetic samples. Sample matrices and concentration levels shall reflect the scope of the standardized analytical method. Particulate matter content shall be sufficient to reflect wastewater samples matrices. Organizers will provide all samples and replicates needed for the interlaboratory trial. No further information about the concentration ranges to be expected in the samples should be given to participants. The interlaboratory trial may be performed with reference materials, if suitable ones are available.

Assigned values for each analyte in the samples should be specified in order to obtain the performance characteristic η (recovery rate). ISO 13528[1] describes different methods of determining the assigned value. The consensus value from participant results is not a suitable assigned value for determining the recovery rate.

Every participant has to perform replicate analyses of each sample according to the overall procedure. Preferably, the number of replicates should not be less than three. The actual number of replicates requested is specified in advance when designing the interlaboratory trial. Therefore, each laboratory shall get the required quantity of sample and/or number of subsamples. Samples shall be distributed in bottles that are unambiguously labelled (e.g. number of sample and subsample, participant and matrix).

The variation in the concentrations of the subsamples should not be excessively increased by the preparation procedure adopted since the reproducibility standard deviation of the test data would otherwise assume unrealistically high values. This should be borne in mind, in particular in relation to unstable and highly volatile analytes.

The stability and homogeneity of subsamples and, in particular, of the substances to be quantified, shall be given at least until the deadline for performance of the analysis. Methods for checking that the samples are adequately homogeneous and stable are given in ISO 13528[1].

Storage conditions (e.g. temperature range, protection from light) are an important point, and compliance with the conditions can be difficult to ensure when shipping the samples to other countries. It is under the responsibility of the organiser to choose a proper way of sample dissemination or distribution.

In addition to the matrix samples, a standard solution or an extract with known but undisclosed concentration should be dispatched as “quality control sample” to check correctness of calibration. If the deviation of the result of this standard solution is bigger than the predefined tolerable deviation, all results from the respective laboratory should be examined in view of discarding from the entire data set.

6.3 Information to be distributed with the samples

The accompanying letter should include the following information:

— the latest version of the standardized analytical method and warning to strictly adhere to this analytical protocol;

— instructions for sample pretreatment and storage conditions;

— additional instructions for performance of analysis, if necessary;

— contact person (project leader or appointed organizer);

— schedule (deadlines for start of analysis and returning results);

— form for results of analysis (unit, number of significant digits etc.);

— questionnaire on experimental details (e.g. clean-up method, chromatography column), especially when testing a multi-option protocol;

— list of data to be handed over, if required (e.g. blank values, calibration data, original chromatograms).

6.4 Statistical evaluation

Before evaluation the result forms from the participants shall be checked for erroneous data. If necessary, the respective participant laboratory should be asked to recalculate their results or check for errors in data transfer.

For approximately continuously measurable analytes, the statistical evaluation shal be performed in accordance with ISO 5725-2. Results reported as “less than” are not valid and shall be excluded from the statistical evaluation.

Results of method options according to 5.2. are pooled.

Data sets are tested for four types of outliers according to the tests described in ISO 5725-2:

a) outlying single result within the independent replicates of one laboratory (Grubbs test);

b) outlying laboratory mean (Grubbs test);

c) outlying within-laboratory variance (Cochran test);

d) the two largest or the two smallest laboratory means are outliers (Grubbs test).

If a “quality control sample” as described in 6.2 was dispatched together with the other samples, the results of this sample should be checked for compliance with the predefined tolerable deviation before starting the statistical evaluation of the analytical results.

NOTE The statistical evaluation according to ISO 5725-2 is only applicable if the analytes are approximately continuously measurable, as is usually the case for chemical and physico-chemical methods.

The results of the statistical evaluation shall be presented as indicated in Clause A.3.

7 Assessment

Different analytical methods lead to different acceptable variation coefficients of reproducibility, dependent on their complexity, the concentration range and the kind and number of sample preparation steps. Generally, the validation of the analytical method was successful if the following criteria are fulfilled:

— for each sample remain at least eight valid data sets (l = 8) after elimination of outliers;

— the percentage of outliers is less than 20 %;

— the variation coefficient of reproducibility $C_{V,R}$ is acceptable. In any case $C_{V,R}$ > 40 % is not acceptable;

— the recovery rate η lies within acceptable limits (e.g. ±30 %).

The experts in charge of the development of the standardized analytical method should specify the acceptable values for $C_{V,R}$ and η, as they are dependent on the analytical method and the analyte to be determined. Results from independent interlaboratory trials for comparable methods and/or parameters can give orientation values.

If one of these criteria is not fulfilled for one or more compounds of the scope, the method is not fit for purpose as a standard for these compounds. It has to be mentioned in the final standard, by specifying this in the scope or by adding an annex with the difficulties / bad results encountered during the interlaboratory trial. A revision of the analytical procedure can necessitate the repetition of the interlaboratory trial.

If the percentage of results reported as “less than” is more than 10 %, the lower limit of application should be reconsidered.

8 Documentation and reporting

Upon completion of the statistical evaluation a certificate of participation showing the laboratory's results and the overall means of results for each sample should be sent to each participant.

A report which includes graphical and tabular presentations of all received results (which are generally made anonymous) may be sent to participants of the interlaboratory trial and to the experts in charge of the development of the standardized analytical method who have to set up the recommendation on the status of the final publication.

Annex A
(informative)

Checklist, timetable and reporting the performance data

A.1 Checklist for design and organization of interlaboratory trials for method validation

The checklist for design and organization of interlaboratory trials for method validation includes the following.

— development of the method and validation of the individual steps have been completed;

— samples for each matrix of the scope;

— concentrations of analytes representing the scope of the standardized analytical method;

— assigned values of the analytes;

— tests for stability and homogeneity of the samples successfully passed;

— shipping requirements clarified;

— at least 12 participants (also for each optional analytical procedure, where applicable);

— information for participants:

  — latest version of the standardized analytical method the interlaboratory trial is based on;

  — requirements (no technical alterations of the given method, the participant should be familiar with the respective method);

  — schedule (performance of analysis, reporting of results);

  — storage conditions for samples;

  — number of replicates;

  — reporting of analytical details and results (form, preferably electronically);

— criteria for exclusion of data from the statistical evaluation.

A.2 Timetable

Table A.1 is an example for a preliminary schedule of an interlaboratory trial.

Table A.1 — Preliminary schedule of an interlaboratory trial

Time	Task
Five months before dispatch of samples	Call for participants, expression of interest within four weeks
Four months before dispatch of samples	Circulation of detailed information about the inter-laboratory trial together with a form for binding registration. Checks for stability and homogeneity of samples