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Water quality — Interlaboratory comparisons for proficiency testing of analytical chemistry laboratories

Qualité de l'eau — Comparaisons interlaboratoires pour des essais de compétence de laboratoires de chimie analytique

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Foreword

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In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

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Introduction

Participation in interlaboratory tests in various test fields offers a testing laboratory an opportunity to obtain an objective picture of its proficiency. Such tests serve as a confidence-building measure both for the laboratory itself and for prospective clients.

This Technical Specification is based on the following international recognized documents:

— ISO/IEC Guides 43-1 and 43-2;

— ISO 13528;

— *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories* – (IUPAC, ISO, AOAC);

— ILAC Guide 13;

— ISO/IEC 17025;

— ISO 5725-1 and ISO 5725-2.

As these documents only define a framework for design, execution and evaluation of proficiency testing by interlaboratory comparisons, this Technical Specification describes in detail an evaluation procedure which is especially suitable for the sector of water, waste water and sludge analysis, where results of interlaboratory comparisons play an important role in the admission of laboratories to certain analytical tasks. Therefore, the fairness of assessment of laboratories must be guaranteed. Assessment should not be dependent on the provider, the date, or the method of evaluation.

Water quality — Interlaboratory comparisons for proficiency testing of analytical chemistry laboratories

1 Scope

This Technical Specification specifies the criteria related to proficiency testing by interlaboratory comparisons in the field of water, waste water and sludge analysis. In particular, it specifies the requirements in respect to proficiency test providers and to the design, execution and evaluation of laboratory proficiency comparisons.

This document may be used if the determinands in the interlaboratory test may be regarded as capable of measurement with a certain degree of continuity. This is generally the case for chemical constituents and physicochemical determinands, but continuity does not always exist in the case of biological and/or microbiological determinands.

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: General statistical terms and terms used in probability*

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

ISO 5725-1:1994/Cor.1:1998, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions — Technical Corrigendum 1*

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 13528, *Statistical methods for use in proficiency testing by interlaboratory comparisons*

ISO/IEC Guide 43-1, *Proficiency testing by interlaboratory comparisons — Part 1: Development and operation of proficiency testing schemes*

ISO/IEC Guide 43-2, *Proficiency testing by interlaboratory comparisons — Part 2: Selection and use of proficiency testing schemes by laboratory accreditation bodies*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO/IEC 17020, *General criteria for the operation of various types of bodies performing inspection*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3534-1, ISO 5725-1, ISO 5725-2, ISO/IEC Guide 43-1, ISO/IEC Guide 43-2 and the following apply.

3.1
breakdown point
smallest percentage of outlier laboratories above which the estimation method may be entirely inapplicable

3.2
efficiency
ratio of the variance of the optimum estimation method for normal distribution to the variance of the estimation method under consideration, each assuming a normal distribution

NOTE This is expressed as a percentage.

3.3
sample
totality of a homogeneous analysis material with an identical composition or quality (similar to term batch)

3.4
subsample
defined portion of a sample obtained by suitable sample division and identical in terms of composition

4 Symbols

d_i	Absolute difference between log-linear variance function and the logarithm of the reproducibility standard deviation
$G_1(x_i)$	Generalized distribution function of interlaboratory differences with continuity correction (s_R)
$G_2(x_i)$	Generalized distribution function of intralaboratory differences with continuity correction (s_r)
g	Quality limit
$H_1(x_i)$	Generalized distribution function of interlaboratory differences (s_R)
$H_2(x_i)$	Generalized distribution function of intralaboratory differences (s_r)
i	Index denoting the serial number of one of p samples
J_i	Number of participants in the case of sample i
j	Index denoting the serial number of one of J participating laboratories
k_1,k_2	Correction factors for calculating z_U-score
μ	Overall mean
μ_i	Overall mean of i-th sample
x_a	Assigned value
n_j	Number of measurements made by laboratory j

q	Quantile parameter
p	Number of samples (levels)
PG_0, PG_1	Testing values for testing variance function
s_R	Reproducibility standard deviation
s_{R_i}	Reproducibility standard deviation of i-th sample
$\hat{s}_{R_i}$	Reproducibility standard deviation for sample i adjusted using a variance function
s_r	Repeatability standard deviation
$\hat{\sigma}$	Standard deviation for proficiency assessment
W	Weighting matrix
X	Design matrix
X^T	Transposed design matrix
x_i	Discontinuity point
y	Arithmetic mean of test results of an unspecified laboratory
y_{ji}	Measurement result for the i-th measurement made by laboratory j
y_j	Arithmetic mean of measurement results of laboratory j
z	z-Score, i.e. standardized deviation of laboratory result from assigned value
z_U	Corrected z-score
Ψ	Function for determining the Hampel estimator
$\chi^2_{p-2;0,95}$	95 % chi-squared quantile for $p - 2$ degrees of freedom
Φ	Distribution function of standard normal distribution
α	Significance level
ν	Relative reproducibility standard deviation
γ	Vector of logarithms of standard deviations
θ_0, θ_1	Parameters of log-linear variance function
$\tilde{\theta}_0$	Estimate of logarithm of relative reproducibility standard deviation if independent from concentration level

5 Requirements relating to proficiency test provider

Proficiency testing by interlaboratory comparisons must lie in the responsibility of specialists who are familiar not only with the requirements relating to the design, execution and evaluation of interlaboratory tests, but also with the analytical methods to be tested, and who have demonstrated their specialist knowledge. Against this background, it is recommended that the test provider regularly organizes interlaboratory tests in the relevant test field.

The proficiency test provider must maintain an adequately documented quality management system based on the criteria specified in ISO/IEC 17020 or ISO/IEC 17025, covering all necessary framework conditions, responsibilities and standard operation procedures.

In addition all measurements within the framework of the provided proficiency test should fulfil the technical requirements as specified in ISO/IEC 17025.

An advisory group that includes specialists for all the fields involved should be appointed to enable the relevant interlaboratory test system to be brought into line with the state of the art and proper account to be taken of the specialist requirements relating to the interlaboratory tests. Keeping a written record of the group's decisions is recommended.

6 Participants

Only laboratories that have the requisite staffing and equipment for the tests to be performed shall take part in an interlaboratory test. Each participating laboratory should appoint a member of staff to be responsible for maintaining contact with the proficiency test manager and ensuring that the analyses are correctly carried out in accordance with the proficiency test manager's instructions.

7 Proficiency test design

7.1 Proficiency test plan

All details of the proficiency test design should be laid down in a plan prior to the start of the interlaboratory test. This includes especially details about:

— involved staff;

— sample matrix;

— determinands to be analysed;

— concentration level of the determinand;

— number of samples;

— sample containers;

— sample preservation;

— distribution of samples;

— communication with participants of the proficiency test (PT);

— homogenization method;

— homogeneity and stability check;

— method for stipulating the assigned value;

— schedule;

— evaluation and assessment procedure.

All relevant practices listed in ISO Guide 43-1 shall be fulfilled.

7.2 Sample selection

In selecting the sample material, account shall be taken of the objectives of the interlaboratory test, the target concentration levels, the required homogeneity and stability of the samples, and the transport and storage facilities. In general, real or spiked real samples shall be given preference over synthetic ones. Sample matrix and concentration levels should reflect routine conditions.

7.3 Selection of determinands

The determinands selected in a particular case and their number shall be defined precisely in accordance with the target group of participants or with the reason for the interlaboratory test. Determinands shall be defined accurately, i.e. whether a certain form (e.g. soluble) or the total concentration shall be determined.

7.4 Spiking

For the preparation of samples, the proficiency test provider may spike samples with low concentrations. This can be a useful way of establishing required combinations of concentrations of individual analytes in samples. However, it does not make sense or may not be possible in all cases, especially if the type of analyte binding in the original sample is significantly different from that in the spiked solutions and the degree of difficulty in performing the analytical methods is altered.

7.5 Number of participants

If statistical methods are used to calculate an assigned value from participants data, the number of participants has an influence on the reliability of the statistically calculated data. In this, it is therefore desirable to ensure that the number of laboratories participating in the interlaboratory tests is sufficiently large and never less than twelve if the assigned value is derived from the participants data.

7.6 Number of samples

Testing several samples for the same analyte yields a more reliable picture of the proficiency of a laboratory and it is therefore desirable for the participants to analyse several samples involving different concentrations of the individual analytes.

Steps shall be taken to ensure that no single participant receives only samples having a high (or low) concentration.

7.7 Multiple determinations and sample size

To ensure that the interlaboratory tests are performed under conditions that resemble routine operation as closely as possible, the participants shall make the same number of multiple determinations as in their routine work. Attention shall be drawn to any specification of the number of parallel determinations required by regulations or by the proficiency test provider.

To reduce the possibility that multiple determinations are not in line with routine or go beyond the number specified in the interlaboratory test, the proficiency test provider should, if practicable, limit the sample size to that required for the specified test.

Dilution of concentrates by the participants prior to testing should be avoided if possible.

8 Execution of proficiency tests

8.1 General

A written record should be kept confirming correct implementation of all the requirements of the proficiency test plan as well as any necessary deviations from the specified procedure.

8.2 Sample preparation

All the steps to be taken in obtaining the sample material, ranging from the selection and cleaning of the transport vessels, sampling and transportation to the laboratory to dispensing, labeling and packaging the subsamples, should be documented in standard operation procedures.

If synthetic samples are prepared or real samples are spiked, the proficiency test provider should provide evidence of the suitability of the materials/substances used in regard to traceability of the chemical composition and the stoichiometry.

All the procedures for ensuring correct spiking, e.g. determination of the pipettes precision or of volume measurements based on mass, should be clearly documented. In addition, contamination and analyte losses should be determined and taken into account. Responsibility for these steps should be specified before the interlaboratory test is started.

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 containers for samples and subsamples should be such as to ensure that contamination resulting from the material and losses due to adsorption, outgassing and the like are minimized.

8.3 Stability and homogeneity testing

The proficiency test provider should provide evidence of the stability and homogeneity of subsamples and, in particular, of the substances to be quantified, for every phase of the interlaboratory test. For this purpose, additional backup samples to be analysed at suitable time intervals during the interlaboratory test by the test provider for the purpose of checking stability should be prepared when dispensing the subsamples.

8.4 Prevention of collusion between participants

Examples of possible steps to be taken by the proficiency test provider to prevent improper contacts are given below:

a) requiring the laboratories to submit copies of the raw data printouts from their analytical equipment along with the analytical results so that the proficiency test manager can use them to perform plausibility tests;

b) each participant receives a subset of the samples prepared (e.g. 3 out of 12);

c) contact accreditation body requiring spot checks to be performed on raw data and other printouts in the course of auditing in the participants laboratory.

8.5 Analytical methods

Depending on the objective or context of the interlaboratory test, the proficiency test provider may restrict or specify the analytical methods to be used. If he does not, the person in charge in the participating laboratory shall use the method normally used by the laboratory for analysing this type of sample.