TECHNICAL SPECIFICATION

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First edition

Water quality — Sampling —

Part 25: Guideline on the validation of the preservation time of water samples

Qualité de l'eau — Échantillonnage —

Partie 25: Lignes directrices pour la validation de la durée de conservation des échantillons d'eau

PROOF/ÉPREUVE

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Foreword

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This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 6, *Sampling (general 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

This document addresses the need for harmonized and reliable data on stability, which is essential for the expression of recommendations for both normative and regulatory purposes. It describes a methodological framework that enables laboratories to produce quality data that can be shared and even monetized[7].

It enables laboratories to study the stability of parameters when using the physico-chemical parameters measurement system: organic micropollutants, inorganic and organometallic micropollutants, nutrients and macropollutants in aqueous matrices (surface water, ground water, residual urban and industrial water and drinking water). It covers the sampling, transport and laboratory storage operations.

NOTE This document does not cover solid matrices from aquatic environments (suspended solids, sediments).

Water quality — Sampling —

Part 25: Guideline on the validation of the preservation time of water samples

1 Scope

The purpose of this document is to describe test plans and different operating methodologies of these test plans to define and verify the acceptable length of stability of a substance in a sample under specified conditions of preservation (temperature, matrix, light, addition of a stabilizer, where appropriate, type of preservation etc.) before starting analytical protocols (chemicals and physico-chemicals analysis). Biological and microbiological methods are excluded.

It is necessary to have an analytical method with performances that have already been characterized (repeatability, intermediate precision, trueness, accuracy and uncertainty) in order to perform the stability study and implement its test plans.

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/TS 21231, *Water quality — Characterization of analytical methods — Guidelines for the selection of a representative matrix*

3 Terms, definitions and symbols

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 https://www.electropedia.org/

For the purposes of this document, the following terms and definitions apply.

3.1
analytical process
detailed description of a measurement according to one or more measurement principles and to one given measurement method, and including any calculations intended to obtain a measurement result

3.2
batch (production, material)
definite amount of test material prepared by the laboratory at a given point in time under supposedly identical conditions

3.3
chronological stability study
study in which individual samples prepared at the same time (i.e., as a batch), under identical conditions, are measured as time elapses (e.g. one sample immediately, one after three months, the next one after six months, etc.)

[SOURCE: ISO Guide 35:2017, 8.3.2.1]

3.4
homogeneity
uniformity of a specified property value throughout a defined portion of a reference material (RM)

Note 1 to entry: Tests for homogeneity are described in ISO Guide 35[2].

Note 2 to entry: The "defined portion" may be, for example, an RM batch or a single unit within the batch.

Note 3 to entry: See also IUPAC Compendium on Analytical Nomenclature[6].

[SOURCE: ISO Guide 30:2015, 2.1.12]

3.5
influence parameter
intrinsic characteristic of the matrix, independent of the analyte concentration, a variation of which is liable to modify the analytical result

[SOURCE: ISO/TS 21231:2019, 3.3.1]

3.6
influence parameter of the conditions of preservation
characteristic related to the conditions of storage and preservation of the sample, independent of the analyte concentration

Note 1 to entry: E.g. container material, storage temperature, influence of light and/or relative humidity.

3.7
integrity
property that the parameter(s) of interest, information or content of the sample container has not been altered or lost in an unauthorized manner or subject to loss of representativeness

[SOURCE: ISO 5667-3:2018, 3.1]

3.8
intermediate precision condition of measurement
condition of measurement, out of a set of conditions that includes the same measurement procedure, same location, and replicate measurements on the same or similar objects over an extended period of time, but may include other conditions involving changes

Note 1 to entry: The changes can include new calibrations, calibrators, operators, and measuring systems.

Note 2 to entry: A specification for the conditions should contain the conditions changed and unchanged, to the extent practical.

Note 3 to entry: In chemistry, the term "inter-serial precision condition of measurement" is sometimes used to designate this concept[8].

3.9
isochronous stability study
experimental study of "reference" material stability in which units exposed to different storage conditions and times are measured in a short period of time

[SOURCE: ISO Guide 35:2017, 3.9]

3.10
matrix
all the constituents of the laboratory sample other than the analyte

Note 1 to entry: By extension, a matrix is defined by the analyst as waters characterized by a homogeneous behaviour with regard to the analytical method used.

[SOURCE: ISO/TS 21231:2019, 3.3.3]

3.11
maximum acceptable delay before analysis (MaxADs)
maximum acceptable delay between the end of the sampling process and the start of the analysis operations, resulting from the stability study, that the laboratory uses to plan the analyses

3.12
maximum acceptable deviation for the stability study (MADs)
maximum acceptable deviation relative to the assigned value of the sample at T_0, used to determine the maximum acceptable delay before analysis

3.13
measurement precision
closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

Note 1 to entry: Measurement precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.

Note 2 to entry: The "specified conditions" may be, for example, repeatability conditions of measurement, intermediate precision conditions of measurement, or reproducibility conditions of measurement (see ISO 5725-1:1994[1]).

Note 3 to entry: Measurement precision is used to define measurement repeatability, intermediate measurement precision, and measurement reproducibility.

Note 4 to entry: Sometimes “measurement precision” is erroneously used to mean measurement accuracy[8].

3.14
measurement repeatability
measurement precision under a set of repeatability conditions of measurement

[SOURCE: JCGM 200:2012 (VIM), 2.21]

3.15
measurement reproducibility
measurement precision under reproducibility conditions of measurement

Note 1 to entry: I.e., condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects.

[SOURCE: JCGM 200:2012 (VIM), 2.25]

3.16
measurement trueness
closeness of agreement between the average of an infinite number of replicates measured quantity values and a reference quantity value

Note 1 to entry: Measurement trueness is not a quantity and thus cannot be expressed numerically, but measures for closeness of agreement are given in ISO 5725-1:1994[3].

Note 2 to entry: Measurement trueness is inversely related to systematic measurement error, but is not related to random measurement error.

Note 3 to entry: “Measurement accuracy” should not be used for ‘measurement trueness’.

[SOURCE: JCGM 200:2012 (VIM), 2.14]

3.17
minimum quantifiable deviation for the stability study (MQDs)
minimum deviation relative to the assigned value of the parameter in the sample at T_0, which can be unequivocally imputed to the instability

Note 1 to entry: This deviation takes account of the inhomogeneity of the test material and the intrinsic variability of all the measurement results over time used to determine the maximum acceptable deviations.

Note 2 to entry: The calculation of the minimum quantifiable deviation for the stability study depends on the type of study (chronological, pseudo-isochronous or isochronous) (6.1.1).

3.18
pseudo-isochronous stability study
stability study in which some of the steps, in particular the preparation, are performed under intermediate precision conditions, and in which the results of instrumental analyses are acquired under repeatability conditions

3.19
repeatability condition
condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

Note 1 to entry: A condition of measurement is a repeatability condition only with respect to a specified set of repeatability conditions.

Note 2 to entry: In chemistry, the term "intra-serial precision condition of measurement" is sometimes used to designate this concept[8].

3.20
representative matrix
sample for which all the intrinsic characteristics are characteristics of a type of water or the source of a group of samples

[SOURCE: ISO/TS 21231:2019, 3.3.2]

3.21
reproducibility condition
condition of measurement, out of a set of conditions that includes different locations, operators, measuring systems, and replicate measurements on the same or similar objects

Note 1 to entry: The different measuring systems may use different measurement procedures.

Note 2 to entry: A specification should contain the conditions changed and unchanged, to the extent practical[8].

3.22
sample preservation
any procedure used to stabilize a sample in such a way that the properties under examination are maintained stable from the collection step until preparation for analysis

[SOURCE: ISO 5667-3:2018, 3.2]

3.23
sample storage
process and the result of keeping a sample available under predefined conditions, usually for a specified time interval between collection and further treatment of a sample

Note 1 to entry: Specified time is the maximum time interval [see ISO 5667-3].

3.24
stability
characteristic of an analyte in an aqueous matrix, when stored under specified conditions, to maintain its property value within specified limits for a specified period from sampling to laboratory operations

3.25
stability interval
interval defined on the basis of the assigned value at T_0 and the maximum acceptable deviation for the stability study

3.26
storage time
period of time between filling of the sample container and further treatment of the sample in the laboratory, if stored under predefined conditions

Note 1 to entry: Sampling finishes as soon as the sample container has been filled with the sample. Storage time ends when the sample is taken by the analyst to start sample preparation prior to analysis.

Note 2 to entry: Further treatment is, for most analytes, a solvent extraction or acid destruction. The initial steps of sample preparation can be steps complementary to the storage conditions for the maintenance of analyte concentrations.

[SOURCE: ISO 5667-3:2018, 3.4]

4 Principle

The goal is to perform a series of tests, hereafter referred to as the "stability study", to analyse the variations in the value of a given parameter, between an initial time and a maximum time, on samples representative of the scope of application of the measurement method of the parameter. The conclusions of these tests are used to determine the maximum acceptable delay before analysis (3.11) under the conditions of the study.

The stability study has six stages:

— Definition of the requirements (analytes, matrices, levels of concentration, storage conditions, length of storage, maximum acceptable deviation for the stability study (3.12)), see Clause 5;

— Definition of the experiments plan (type of study, number of time intervals and total length of the study), see Clause 6;

— Performance of the tests, see Clause 7;

— Validation of the data, see Clause 9;

— Using the results (based on a maximum acceptable deviation, 3.12), see Clause 10;

— Expression of the stability in the form of a maximum acceptable delay before analysis (3.11) and the duration of stability corresponding to the conditions and the criteria (maximum acceptable deviation for the stability study (3.12)) of the study, see Clause 10.

Since the stability study covers different stages of the data acquisition process according to the organization of the measurement system, examples of the organization of the measurement system are given in Annex A for reference.

The laboratory shall take the following factors into consideration:

— The method of determination used: for example, limit of quantification, repeatability, intermediate precision, accuracy, influence parameters of the matrix (3.10) on the performance of the method;

— The "sample" material of the stability study: for example, homogeneity, physico-chemical properties;

— Suitability of the sample material for use as test material in accordance with storage time (3.26).

— Definition of the influence parameters of the preservation conditions (3.6) assessed as part of the stability study: for example, time, temperature, addition of stabilizers;

— If studied, command of the storage and transportation conditions;

— Clearly defined acceptability criteria (maximum acceptable deviation, 3.12), with which the results of the study will be compared.

5 Definition of the scope of the stability study

5.1 Aim of the stability study

Based on the scope of application of the method, the experimental plan shall clearly define the aim of the stability study by specifying the measured analytes, the matrices (3.10) and the target concentration levels.

5.2 Selection of the maximum acceptable delay before analysis and the acceptance criteria

Respecting the maximum acceptable delay before analysis (3.11) may determine the quality of the results of the analysis more than certain performance data of the measurement methods (bias). This is the reason why the maximum acceptable delay before analysis shall be established and known before the routine application of a laboratory analysis method.

The assessment of the results of a stability study with the intension of drawing a conclusion on the stability, expressed as a maximum acceptable delay before analysis, of a given analyte in a representative matrix of the scope of application shall be based on the interpretation of the results in perspective of the requirements of the stability study. A maximum acceptable deviation (3.12) shall be set in order to come to a conclusion. This maximum acceptable deviation shall be chosen before the start of the study, because it determines the conditions of performance of the method and the admissibility of the data, in particular with regard to the measurement method.

There are five ways to determine the maximum acceptable deviation. They are, in order of relevance:

a) The application of a regulatory requirement, if one exists;

b) Twice the repeatability standard deviation for isochronous or pseudo-isochronous type 1 studies (Annex B), or twice the intermediate precision standard deviation for type 2 pseudo-isochronous studies (Annex B) or chronological studies; the values of the standard deviation of repeatability and intermediate precision being the values defined during the characterization of the method.

c) Use of the data from the stability study: dispersion at T_0 of the stability study. See Formula (1):

$$\text{Maximum acceptable deviation} = \text{Minimum quantifiable deviation} \quad (1)$$

d) The choice of an arbitrary value, determined according to the technical operational implementation constraints (e.g., the best available method offering a precision of 15 %) or a value from a CIL (ISO 5667-3). In this case, the maximum acceptable deviation shall be greater than this value, e.g., 25 %.

e) A value derived from the temporal operational implementation constraints (e.g., the impossibility of performing an analysis before a given time due to the minimum transportation time). In this case, the maximum acceptable delay before analysis is fixed and the maximum acceptable deviation is based on the observations at the pre-determined time.

EXAMPLE If the temporal constraint is three days, (MaxADs =3 days) the maximum acceptable deviation is estimated according to the observations (dispersion, for example) at T_3.

If the minimum quantifiable deviation is greater than the maximum acceptable deviation, it is impossible to draw any conclusions about the stability. In this case, the laboratory should identify the causes (e.g., lack of homogeneity of the materials, lack of performances of the method, need to stabilize the materials) and repeat the study (e.g., with a different maximum acceptable deviation, another method, etc.).

5.3 Influence parameters of the maximum acceptable delay before analysis

This protocol applies to conditions clearly defined by the laboratory, which defines the maximum acceptable delay before analysis, the corresponding assessment criterion (see 5.2) and the factors likely to impact it.

In particular, these factors may include:

— The container: ISO 5667-3 or the analysis standards applicable to the targeted parameters specify the recommended containers for the transportation of samples based on current knowledge. However, for certain classes of molecules, for which no normative guidelines exist, the compatibility of these general recommendations on the container material (plastic, glass, etc.) that may cause losses by adsorption, diffusion, the transfer of additives used in production, etc., should be verified;

— The storage temperature (ambient, refrigeration, freezing, etc.), which can impact the partition of the substances between the dissolved and particulate phases, or the enantiomer form, or their biological deterioration. ISO 5667-3 recommends that samples be preserved at 5 ± 3 °C during transportation. Therefore, this temperature range is the reference temperature of the study, in the absence of any other requirements. Other temperatures may be chosen for the study, for example when demonstrating the stability of analytical extracts in the laboratory. The temperature conditions of the study shall be clearly indicated, and they shall be monitored and documented throughout the stability study;

— The influence parameters of the matrix: pH, suspended solids, etc;

— Light, which can cause the photodegradation of certain organic molecules, e.g.: Benzo[a]pyrene, BDE209;

— The influence of sample pre-treatment on site, e.g. filtration[15];

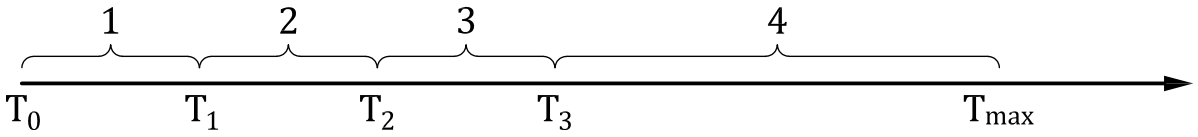
— The addition to the sample of stabilizing chemical agents (e.g., acid for metals, sodium hydroxide for cyanides, solvents, etc.).

5.4 Duration of the study

The duration of the study shall cover the initially planned maximum acceptable delay before analysis. The extrapolation of the MaxADs beyond T_{max} is not permitted. It is thus recommended to collect data beyond the planned MaxADs,

Interpolation between the two terminals of a period of time is not permitted in order to define the maximum acceptable delay before analysis. Therefore, it is recommended to acquire additional information at different intermediate lapses of time.

The laboratory shall adapt the number of the lapses of time (Figure 1) of the study according to its initial knowledge of the stability of the analyte of concerned in order to minimize the risk of inconclusive studies.



Key

1 time lapse 1
2 time lapse 2
3 time lapse 3
4 time lapse 4

Figure 1 — Example of a diagrammatic illustration of the notion of time laps

5.5 Concentration levels

The p tested levels of concentration are chosen according to the requirements of the corresponding sector of activity, any regulatory requirements that may exist, the occurrence of data in the environment, for example, and the performances of the analytical method and its scope of application.

The experimental plan selects one of the two following approaches, depending on the complexity of the matrices and their knowledge of the method:

— At least two levels of concentration ($p \geq 2$) by representative sample ($n \geq 2$) of the matrix of the scope of application of the method shall be considered:

  — One low concentration level, different from the LOQ, ≤ 25 % of the scope of the method for one-decade methods or ≤ 10 % for more-decades methods,

  — One high concentration level, in the second half of the scope of application of the method.

— A minimum concentration level of $p = 1$, ≤ 25 % of scope of the method for one-decade methods, resp. ≤ 10 % for more-decades methods, with several representative samples of the matrix ($p \times n \geq 4$). In this case two time laps should be taken.

The laboratory shall substantiate its choice of n=2 by demonstrating that its scope of application is restricted and, therefore, sufficiently described by two representative samples, in accordance with ISO/TS 21231.

NOTE 1 Performing stability studies at the limit of quantification (LOQ) is not generally relevant. The uncertainty of the methods at the LQ does not allow for the unequivocal interpretation of the data.

NOTE 2 When representative samples free of any background contamination of analyte cannot be found, the environmental background noise should be considered to determine the lowest level of contamination tested in the stability study.

5.6 Definition of the matrices and selection of the representative samples

The experimental plan defines the matrices or group of matrices for the study by referring to ISO/TS 21231. Consequently, the analyst selects representative samples of these matrices or group of matrices. The laboratory shall substantiate its choice.

The representativeness of the samples for the stability study is critically important. Two strategies can be considered:

— the use of natural samples, or

— the use of synthetic samples, which are natural samples whose physico-chemical characteristics are varied using the recipes in ISO/TS 21231; or the addition of influence parameters.

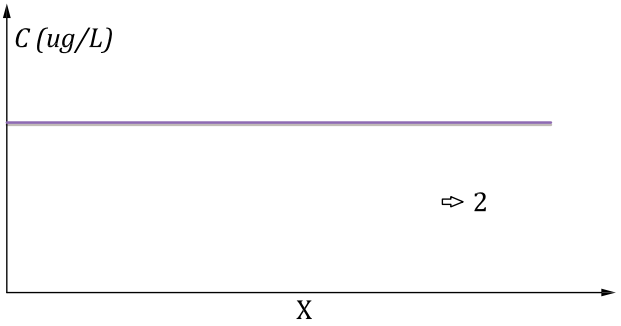
Each type of matrix in the scope of application of the method shall be studied. The influence parameters of each sample shall be measured and recorded at least at T_0.

To guarantee the representativeness of the study and cover the entire range of the influence parameters of the matrix for the parameter(s) of interest, these samples shall have different intrinsic characteristics by type of matrix (surface water, ground water, for example), and include the extreme values of the influencing parameters. For example, the content of suspended solids and the pH for the methods used to analyse organic analytes, or the content of suspended solids and the conductivity for nutrients (see ISO/TS 21231).

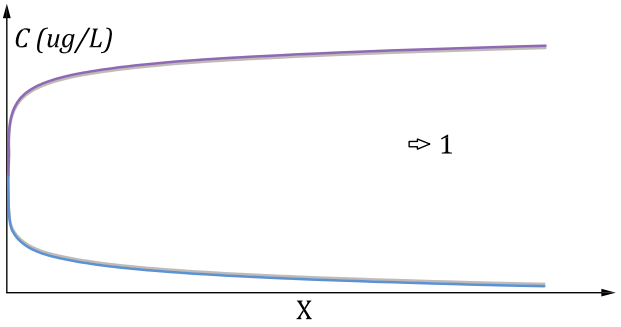
5.7 Guidelines to the stability studies of transformation products

Whenever a stability study is made of a parameter that is known to be a transformation product (metabolite, by-products of oxidation or hydrolysis, for example) of a parent compound (analyte) that may be present in the sample, it is imperative to include the measurement of the parent compound (analyte) in the stability assessment of the transformation product. Transformation products usually have longer half-lives than the parent compound. Consequently, the stability study may erroneously conclude to the stability (Figure 2, a) of the transformation product. In real sample, where the parent compound is present, stability study will lead to instability conclusion of the transformation product together with the parent compound (Figure 2, b).

2a) Stability study – parent compound



2b) Stability study – transformation product (alone)



2c) Stability study – parent compound/transformation product mixtures