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Water quality — Characterization of analytical methods — Guidelines for the selection of a representative matrix

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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

This document has been prepared for the validation of analytical methods applied to the water quality field. It enables a laboratory to determine the characteristics of a material suitable for determination of the performances of an analytical method itself.

It is not intended to provide an exhaustive inventory of all published recipes, but to propose a selection of recipes supporting the characterization of the performances of analytical methods used by a laboratory. For this reason, a restricted number of recipes are proposed. References giving access to other recipes are available in the Bibliography.

This document includes four recipes for preparing marine waters and five recipes for waste waters with controlled characteristics.

Water quality — Characterization of analytical methods — Guidelines for the selection of a representative matrix

1 Scope

This document specifies representative materials suitable for the determination of the performance characteristics, including uncertainty, during the initial assessment of a quantitative method, used in a laboratory, for physico-chemical water analysis.

This document focuses on five main types of water:

— waters intended for consumption (5.2);

— natural waters (5.3);

— waste waters (5.4);

— marine waters (5.5);

— recreational waters (5.6).

NOTE Other more specific or less common types of water can be incorporated in any of the above types provided appropriate justifications. The characteristics of the standard matrix are compatible with the characteristics of the samples handled.

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 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 6107 (all parts), *Water quality — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6107 (all parts) and the following 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 General vocabulary

3.1.1
matrix
set of constituents of the test sample, except the *analyte* (3.2.1)

Note 1 to entry: By extension, a matrix defines a group of waters characterized by similar analytical behaviour in relation to the analytical method used.

3.1.2
accepted reference value
value that serves as an agreed-upon reference for comparison, and which is derived as:

a) a theoretical or established value, based on scientific principles;

b) an assigned or certified value, based on experimental work of some national or international organization;

c) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group;

d) when a), b) and c) are not available, the expectation of the (measurable) quantity, i.e. the mean of a specified population of measurements

Note 1 to entry: In the specific context of this document, the accepted reference value (or conventionally true value) of the sample is provided according to possibilities by:

— the value from a certified reference material certificate,

— the consensus value obtained from an inter-laboratory comparison,

— the arithmetic mean of the repeated measurement values according to the reference method,

— the target value by adding analyte to a representative matrix of the scope in question.

[SOURCE: ISO 5725-1:1994, 3.5]

3.1.3
reference material
material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process

[SOURCE: ISO Guide 35:2017, 3.1]

3.1.4
certified reference material
reference material (3.1.3), accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence

[SOURCE: ISO/TS 13530:2009, 3.2.7]

3.1.5
assessment procedure
procedure related to the establishment of the specifications for the performance of a new method and/or experimental verification that a method meets theoretically derived quality criteria

3.2 Terms related to analytical methods

3.2.1
analyte
subject of the analytical method

3.2.2
analytical method
unambiguously written procedure describing all details required to carry out the analysis of the *analyte* (3.2.1), namely: scope and field of application, principle and/or reactions, definitions, reagents, apparatus, analytical procedures, calculations and presentation of results, performance data and test report

[SOURCE: ISO/TS 16489:2006, 3.3]

3.2.3
quantitative analytical method
analytical method for measuring the quantity of *analyte* (3.2.1)contained in the test sample

Note 1 to entry: The result can consist of a quantity in a given quantity of test sample.

3.2.4
limit of detection
output signal or value above which it can be affirmed, with a stated level of confidence, for example 95 %, that a sample is different from a blank sample containing no determinand of interest, and which could be estimated by different means and shall be verified in the intended matrix

[SOURCE: ISO 6107-2:2006, 60, modified — "and which could be estimated by different means and shall be verified in the intended matrix" has been added.]

3.2.5
limit of quantification
LOQ
lowest value of a determinand that can be determined with an acceptable level of accuracy, which could be estimated by different means and shall be verified in the intended matrix

Note 1 to entry: For each matrix, this limit is related to the pair [*analyte* (3.2.1), method].

3.2.6
reasonable dilution
dilution conditions for reducing the concentration of a substance in a matrix without substantially modifying the intrinsic characteristics of the matrix

3.2.7
matrix blank values
values of a given parameter obtained using a test conducted on a matrix giving rise to a result below the *limit of detection* (3.2.4) for the *analyte* (3.2.1) in question

3.2.8
scope of the analytical method
combination of the various types of matrix and the *analyte* (3.2.1) concentration range covered, to which the analytical method applies

Note 1 to entry: In addition to an indication of all the satisfactory performance conditions for each factor, the scope of the analytical method may also include warnings in respect of known interferences from other analytes, or inapplicability to some matrices or conditions.

3.3 Terms related to matrix

3.3.1
influence parameter
intrinsic characteristic of the matrix, independent of the *analyte* (3.2.1) concentration, a variation of which is liable to modify the analytical result

3.3.2
representative matrix
sample for which all the intrinsic characteristics are characteristic of a type of water or the source of a group of samples

3.3.3
salinity
mass in grams of solid substances contained in one kilogram of sea water, when the bromide and iodide ions are replaced by their chloride equivalent, carbonates converted into oxides and all the organic matter oxidized

3.3.4
leachate
water which has percolated through tipped refuse or other specified permeable material

Note 1 to entry: See Annex D.

[SOURCE: ISO 6107-7:2006, 23]

4 Principle

The purpose of this document is to specify the concept of a representative matrix and its characteristics with a view to studying the performance of an analytical method.

For each analyte under test, the scope of an analytical method includes all the matrices under test, their descriptive parameters, and the concentration ranges of the influence parameters for which the method is applicable. The laboratory should define its requirements beforehand in respect of the scope of the analytical method, selecting the materials most in line with requirements.

WARNING — The definition of the scope is entirely dependent on the analyst (the validation or characterization study manager) and their knowledge acquired while developing the method. It is sometimes preferable to segment a scope rather than seek to validate an overly general method. In this case, a validation file should be compiled for each scope.

See Figure 1.

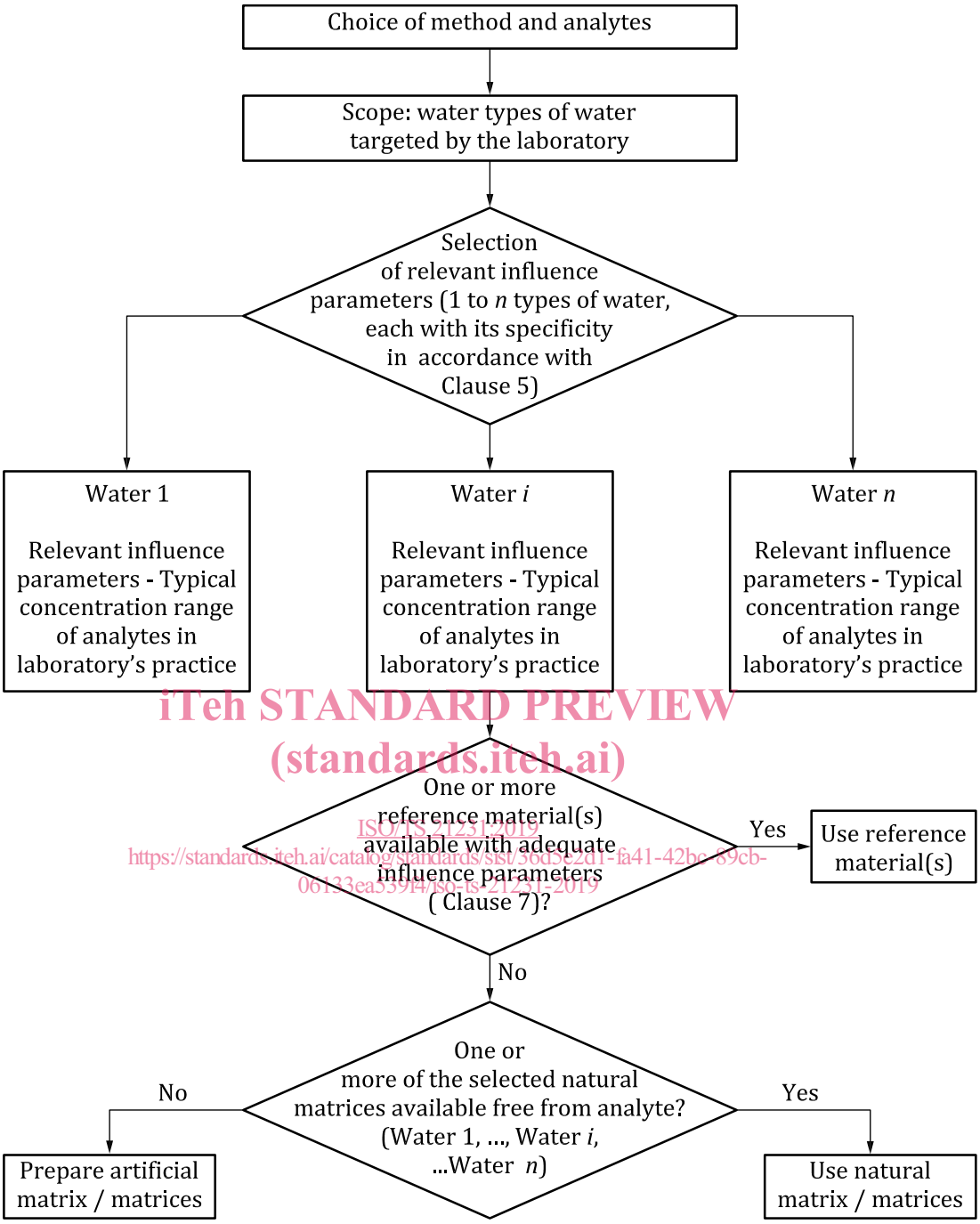

Figure 1 — Summary flow chart

5 Influence parameters

5.1 Common parameters for all matrices

The following influence parameters are liable to have an impact on analysis procedures. They shall help classify the types of water on which the laboratory has validated its method or determined performance characteristics.

— pH;

— ion composition and/or conductivity;

— salinity;

— dissolved organic carbon (DOC) and/or total organic carbon (TOC);

— colour or turbidity;

— suspended particular matter (SPM) content.

During the validation or characterization study, it is up to the laboratory to:

— define, for its practice, the characteristic ranges associated with each of the above parameters;

— justify, if applicable, the lack of influence thereof on the characterized method;

— complement this list with other characteristic parameters based on the methods and the source of the samples analysed, using for example Annex A or Annex C.

5.2 Water intended for consumption

Water intended for human and livestock consumption is water considered to be fit for drinking.

Drinking water belongs to this category. It includes groundwater that has been chlorinated in the resource.

The minimum additional characteristics to be included for this category are:

— disinfectant presence and content (distributed waters or groundwater chlorinated in the resource);

— CO_2 content (natural mineral water), if relevant to subsequent specified analysis requirements.

5.3 Natural waters

Natural waters are waters taken from the natural environment not undergoing to any treatment other than the addition of reagents for analyte preservation.

Surface waters and groundwater belong to this category. Brackish waters with salinity lower than 30 g/l are incorporated in this category.

Rainwater, which is generally not intended for consumption, are incorporated in this category.

5.4 Waste waters

Waste waters can originate from any combination of household, industrial or commercial activities. They include collected run-offs and those from any spillage or infiltration from the waste water collection system, including the contents of storm water tanks or ponds, discharged into collection systems or into the environment.

NOTE 1 Waste waters can be collected in common systems or in separate systems.

NOTE 2 For the purposes of this document, the definition of waste water also includes untreated sanitary waters.

NOTE 3 National or local regulations can include lists of substances of concern in relation to sewer discharges.

Annex C gives a list of examples of additional characteristics associated with some sectors of activity.

Some waste waters may have a high salinity.

5.5 Marine waters

Sea water consists of a large number of compounds distributed over the following categories: gases, particulate matter, colloids, and dissolved elements (see Reference [7]).

The dissolved elements consist of 92 natural chemical elements, approximately two-thirds of which are present in ultra-trace amounts and are difficult to detect. Sea water is characterized in that the relative proportions of its 11 main constituents are substantially constant (Dittmar's law [8]) within 1 %. Dittmar's law can thus be used to determine the salinity of sea water by measuring only one of its components.

The average salinity of sea water is 35 g/kg. It is generally between 30 g/kg (North Atlantic) and 40 g/kg (Red Sea) but exhibits extreme values in closed or semi-closed seas (6 g/kg in the Baltic Sea, 330 g/kg in the Dead Sea). The pH of sea water is approximately 8,2.

5.6 Recreational waters

Recreational waters are bathing, swimming pool, thermal bath and spa waters. They may be sourced from natural waters or waters intended for human consumption and are characterized, in addition to the influence parameters defined in 5.2, by the potential presence of specific disinfection products and by-products, and the potential presence of sulfur compounds.

6 Selection of characteristic parameters of a matrix

6.1 General

For the purposes of characterization of the applicability and the performances of an analytical method to a matrix, the laboratory shall describe the limits of the ranges associated with the characteristic parameters discussed in this clause.

6.2 All waters

The parameters are those defined in 5.1.

6.3 Waters intended for consumption

In addition to the characteristics listed in 5.1, waters intended for consumption are characterized by:

— their free and total chlorine content;

— the nature and content of disinfection reagents and by-products;

— their CO_2 content, if relevant.

Refer to Annex A for more detailed characterization of waters intended for human consumption.

6.4 Natural waters

In addition to the characteristics listed in 5.1, natural waters are characterized by:

— the sampling location, including the sampling depth;

— the identified surrounding anthropic pressures.

In the case of groundwater used as drinking water resources, which are treated in situ, free and total chlorine content should be verified.

6.5 Waste waters

In addition to the characteristics listed in 5.1, waste waters are characterized by:

— the original activity sector (see Annex C);