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Water quality — Sampling —

Part 3:
Preservation and handling of water samples

Qualité de l'eau — Échantillonnage —

Partie 3: Conservation et manipulation des échantillons d'eau

[Revision of third edition (ISO 5667-3:2003)]

ICS 13.060.45

ISO/CEN PARALLEL PROCESSING

This draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO-lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five-month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

In accordance with the provisions of Council Resolution 15/1993 this document is circulated in the English language only.

Conformément aux dispositions de la Résolution du Conseil 15/1993, ce document est distribué en version anglaise seulement.

To expedite distribution, this document is circulated as received from the committee secretariat. ISO Central Secretariat work of editing and text composition will be undertaken at publication stage.

Pour accélérer la distribution, le présent document est distribué tel qu'il est parvenu du secrétariat du comité. Le travail de rédaction et de composition de texte sera effectué au Secrétariat central de l'ISO au stade de publication.

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 5667-3 was prepared by Technical Committee ISO/TC 147, *Water Quality*, Subcommittee SC 6, *Sampling*.

This fourth edition cancels and replaces the third edition (ISO 5667-3:2003), which has been technically revised.

ISO 5667 consists of the following parts, under the general title *Water Quality — Sampling*:

— Part 1: Guidance on the design of sampling programmes and techniques

— Part 3: Preservation and handling of water sample

— *Part 4: Guidance on sampling from lakes, natural and man-made*

— *Part 5: Guidance on sampling of drinking water and water used for food and beverage processing*

— *Part 6: Guidance on sampling of rivers and streams*

— *Part 7: Guidance on sampling of water and steam in boiler plants*

— *Part 8: Guidance on the sampling of wet deposition*

— *Part 9: Guidance on sampling from marine waters*

— *Part 10: Guidance on sampling of waste waters*

— *Part 11: Guidance on sampling of groundwaters*

— *Part 13: Guidance on sampling of sludges from sewage and water-treatment works*

— *Part 14: Guidance on quality assurance of environmental water-sampling and handling*

— *Part 15: Guidance on preservation and handling of sludge and sediment samples*

— *Part 16: Guidance on biotesting of samples*

— *Part 18: Guidance on sampling of groundwater at contaminated sites*

— *Part 19: Guidance on sediment sampling in marine areas*

— *Part 20: Guidance on the use of sampling data for decision making - Compliance with thresholds and classification systems*

— *Part 21: Guidance on sampling of drinking water distributed by non-continuous, non-conventional means*

— *Part 22: Guidance on design and installation of groundwater sample points*

The following part is in preparation:

— *Part 23: Determination of significant pollutants in surface waters using passive sampling*

Introduction

This part of ISO 5667 is intended to be used in conjunction with ISO 5667-1, which deals with the design of sampling programmes and sampling techniques.

Where possible this standard has been brought into line with existing, current standards. Where new research or validation results have provided new insights, the latest knowledge has been used.

Guidance on validation protocols can be found in ISO Guide 34

Water quality — Sampling —

Part 3: Preservation and handling of water samples

1 Scope

This part of ISO 5667 establishes general principles for sampling, preservation, handling, transport and storage of all water samples including those for biological analyses, but not those intended for microbiological analysis, ecotoxicological assays and passive sampling as described in the scope of ISO 5667-23.

This standard is particularly appropriate when spot or composite samples cannot be analyzed on site and have to be transported to a laboratory for analysis.

The preservation techniques specified in this International Standard are applicable if there are no contradictory requirements concerning the preservation of samples in the analytical method intended to be carried out after the completion of the procedures described. Differing preservation requirements of analytical methods may be tailored to the particular requirements of the specific analytical method. Contradictory requirements shall be the result of changes in analytical techniques and standards The reason for particular deviation shall be noted in the most recent analytical method standard.

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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 15913, *Water quality — Determination of selected phenoxyalkanoic herbicides, including bentazones and* hydroxybenzonitriles *by gas chromatography and mass spectrometry after solid phase extraction and derivatization*

ISO 19458, *Water quality — Sampling for microbiological analysis*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in the ISO 6107-series and the following apply.

3.1
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

[ISO 11074:2005, 4.4.20]

NOTE Different analytes may require several samples from the same source that are stabilized by different procedures.

3.2
sample storage
process, and the result, of keeping a sample available under predefined conditions for a (usually) specified time interval between collection and further treatment of a sample

[ISO 11074:2005, 4.4.22]

NOTE Specified time is the maximum time interval.

3.3
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. Sampling finishes as soon as the sample container has been filled with sample. Storage time ends when the sample is taken by the analyst to start sample preparation prior to analysis

NOTE Further treatment, is for most of the analytes, a solvent extraction or acid destruction. The initial steps of sample preparation, may be steps complementary to the storage conditions for the securing of analyte concentrations.

4 Sampling

If there is a need to take samples this will be done according a sampling programme. The first step is to design a sampling programme. Guidance on this topic is given in ISO 5667-1.

Depending on the sample type and matrix, guidance can be found in the different ISO 5667-documents and ISO 19458.

The process of preservation and handling of water samples consists of several steps. During this process, the responsibility for the samples might change. To ensure the integrity of the samples, it is vital that all steps involving the sample be documented.

5 Handling and preservation of samples

5.1 Reagents and materials

WARNING — Certain preservatives (e.g. acids, alkalis, formaldehyde) need to be used with caution. Sampling personnel should be warned of potential dangers, and appropriate safety procedures should be followed.

The following reagents are used for the preservation of samples and shall only be prepared according to individual sampling requirements. Unless otherwise specified, all reagents used shall be of at least analytical reagent grade and water shall be of at least ISO 3696 Grade 2 purity. Acids referred to in this part of ISO 5667 are commercially available “concentrated” acids.

All reagents shall be labelled with a “shelf life”. The “shelf life” represents the period for which the reagent is suitable for use, if stored correctly. This “shelf life” shall not be exceeded. Any reagents that are not completely used by the expiry of the “shelf life” date shall be discarded.

Check the reagent dispensers periodically and discard any reagent where dispensers are shown to be unsuitable.

Between field trips, reagents shall be stored in clean, secure cabinets in order to prevent contamination.

Each sample shall be labelled accordingly, after the addition of the preservative. Otherwise, there may be no visible indication as to which samples have been preserved, and which have not.

5.1.1 Solids

5.1.1.1 Sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$

5.1.1.2 Ascorbic acid, $C_6H_8O_6$

5.1.1.3 Sodium hydroxide, NaOH

5.1.1.4 Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$

5.1.1.5 Hexamethylenetetramine (hexamine, urotropine), $C_6H_{12}N_4$

5.1.1.6 Potassium iodide, KI

5.1.1.7 Iodine, I_2

5.1.1.8 Sodium actetate, $C_2H_3NaO_2$

5.1.2 Solutions

5.1.2.1 Zinc acetate solution (r = 0,10 g/ml), $C_4H_6O_4Zn$

5.1.2.2 Orthophosphoric acid (r = 1,7 g/ml), H_3PO_4

5.1.2.3 Hydrochloric acid (r = 19 g/ml), HCl

5.1.2.4 Nitric acid (r = 1,42 g/ml), HNO_3

5.1.2.5 Sulfuric acid (8 mol/l), H_2SO_4

5.1.2.6 Sodium hydroxide solution (r = 0,40 g/ml), NaOH

5.1.2.7 Formaldehyde solution (volume fraction of 37 %) (Formalin), CH_2O

WARNING — Beware of formaldehyde vapours. Do not store large numbers of samples in small work areas.

5.1.2.8 Aqueous solution of disodium salt of ethylenediaminetetraacetic (EDTA) (r = 0,025 g/ml), $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$

5.1.2.9 Ethanol (volume fraction of 96 %)

5.1.2.10 Alkaline Lugol solution, 100g Potassium iodide (5.1.1.6), 50 g Iodine (5.1.1.7) and 250 g Sodium acetate (5.1.1.8) in 1 000 ml water to pH 10

5.1.2.11 Acid Lugol solution, 100g Potassium iodide (5.1.1.6), 50 g Iodine (5.1.1.7) and 100 ml acetic acid glacial (5.1.2.17) in 1 000 ml water, to pH 2

5.1.2.12 Formaldehyde Solution, 37 % formaldehyde neutralized with sodium tetraborate or hexamethylene-tetramine (100 g/l formalin solution) to give a final solution of 3,7 % formaldehyde

5.1.2.13 Ethanol preservative solution, at least 70 % by volume fraction ethanol, 37 % by volume fraction and glycerol (in the proportions 100:2:1 respectively).

5.1.2.14 Sodium hypochlorite (mass fraction of 10 %), NaOCl

5.1.2.15 Potassium iodate (mass fraction of 10 %), KIO_3

5.1.2.16 Methanoic acid (formic acid) (volume fraction of > 98%) CH_2O_2

5.1.2.17 Acetic acid glacial $C_2H_4O_2$

5.1.3 Materials

5.1.3.1 Container - Type and volumes specified in Table 1-3

5.1.3.2 Filter – pore size 0.40 - 0.45 µm

5.2 Container selection and preparation

The choice of sample container (5.1.3.1) is of major importance and ISO 5667-1 provides some guidance on this subject.

Details of the type of container used for the collection and storage of samples are given in Tables 1-3. The same considerations given to this selection of suitable container material shall also be given to the selection of cap-liner materials.

Sample containers shall be made of a material appropriate for preserving the natural properties of both the sample and the expected range of contaminants. Suitable types of containers for each analyte to be measured are given in Tables 1-3.

If the samples are to be frozen, suitable containers, such as polyethylene or polytetrafluoroethylene (PTFE), shall be used to prevent breakage.

If disposables are available, these shall be used. Some manufactures will supply containers with a certificate of cleanliness. Such containers shall never be cleaned or rinsed, provided the manufacturer supplies the containers with caps attached.

All preparation procedures shall be validated to ensure positive or negative interferences do not occur. As a minimum, this shall include the analysis of blanks and/or samples containing known levels of relevant analytes.

5.3 Filling the container

The container (5.1.3.1) shall be filled completely unless prescribed differently in the Tables 1-3. If the samples are to be frozen as part of their preservation, sample containers shall not be completely filled, to prevent breakage.

5.4 Handling and preservation of samples for physical and chemical examination

Waters, particularly fresh waters, waste waters and groundwaters, are susceptible to changes as a result of physical, chemical or biological reactions which may take place between the time of sampling and the commencement of analysis. The nature and rate of these reactions are often such that, if precautions are not taken during sampling, transport and storage (for specific analytes), the concentrations determined shall be different to those existing at the time of sampling.

The extent of these changes is dependent on the chemical and biological nature of the sample, its temperature, its exposure to light, the nature of the container in which it is placed, the time between sampling and analysis, and the conditions to which it is subjected, e.g. agitation during transport. Further specific causes of variation are as follows:

a) The presence of bacteria, algae and other organisms can consume certain constituents of the samples. These organisms can also modify the nature of the constituents to produce new constituents. This biological activity affects, for example, the concentrations of dissolved oxygen, carbon dioxide, compounds of nitrogen, phosphorus and, sometimes, silicon.

b) Certain compounds can be oxidized either by dissolved oxygen present in the samples, or by atmospheric oxygen (e.g. organic compounds, Fe (II) and sulfides).

c) Certain substances can precipitate out of solution [for example calcium carbonate, metals and metallic compounds such as $Al(OH)_3$, or can be lost to the vapour phase (for example oxygen, cyanides and mercury).

d) Absorption of carbon dioxide from air can modify pH, conductivity and the concentration of dissolved carbon dioxide. Passage of compounds like ammonia and silicon fluoride through some types of plastics may also affect pH or conductivity.

e) Dissolved metals or metals in a colloidal state, as well as certain organic compounds can be irreversibly adsorbed onto the surface of the containers or solid materials in the samples.

f) Polymerized products can depolymerize, and conversely, simple compounds can polymerize.

Changes to particular constituents vary both in degree and rate, not only as a function of the type of water, but also, for the same water type, as a function of seasonal conditions.

It should be emphasized that these changes are often sufficiently rapid to modify the sample considerably in a short time. In all cases, it is essential to take precautions to minimize these reactions and, in the case of many analytes, to analyze the sample with a minimum of delay. If the required precaution for changes is filtration on site, then a filter (5.1.3.2.) shall be used.

5.5 Handling and preservation of samples for biological examination

The handling of samples for biological examination is different from that for samples requiring chemical analysis. The addition of chemicals to the sample for biological examination is used for either fixation and/or preservation of the sample. The term “fixation” is used to describe the protection of morphological structures, while the term “preservation” is used for the protection of organic matter from biochemical or chemical degradation. Preservatives, by definition, are toxic, and the addition of preservatives may lead to the death of living organisms. Prior to death, irritation may cause the most delicate organisms, which do not have strong cell walls, to collapse before fixation is complete. To minimize this effect, it is important that the fixation agent enters the cell quickly. Some preservatives, for instance, acid solutions of Lugol (5.1.2.11), may lead to the loss of some taxonomical groups of organisms, which can be a problem during certain parts of the year in certain areas. In that case an additional preservative, such as alkaline solutions of Lugol (5.1.2.10), shall be added, for example, in the summer period when the appearance of silico-flagellates may be frequently observed.

The fixing and/or preservation of samples for biological examination shall meet the following criteria:

a) the effect of the fixative, and/or preservative, on the loss of the organism shall be known beforehand;

b) the fixative or preservative shall effectively prevent the biological degradation of organic matter at least during the storage period of the samples;

c) the fixative, and/or preservative, shall enable the taxonomical groups of organisms to be adequately studied during the storage period of the samples.

5.6 Handling and preservation of samples for radiochemical analysis

WARNING — Safety precautions and shielding depend on the activity of the sample.

There is little difference between the handling of samples for radiochemical analysis and the handling of samples for physico-chemical analysis. Safety precautions depend on the nature of the radioactivity of the sample. The preservation techniques for these samples depend on the type of emitter and the half-life of the radionuclide of interest.

6 Sample transport

Cooling or freezing procedures shall be applied to samples to increase the time period available for transport and storage and if required by tables 1-3. When transport takes place the sampling (plan) shall consider the total time between sampling and start of analysis in the laboratory, the storage time and the degree of representativeness of the sample which may be limited by maximum storage times according to table1-3 or cost or convenience.

A cooling temperature during transport of (5 ± 3) ^{o}C has been found suitable for many applications. Cooling and freezing procedures applied shall be in line with instructions from the analytical laboratory. Freezing especially requires detailed control of the freezing and thawing process in order to return the sample to its initial equilibrium after thawing.

NOTE Cool boxes and freezer packs are capable of at least maintaining the temperature of the sample during sampling during transport.

Containers holding samples shall be protected and sealed during transport in such a way that the samples do not deteriorate or lose any part of their content. Container packaging shall protect the containers from possible external contamination, particularly near the opening, and should not itself be a source of contamination.

Glass containers shall be protected from potential breakage during transport by appropriate packaging. Samples shall be transported as soon as possible after sampling and with cooling if necessary according to Table 1-3.

Laboratory samples for dispatch or transport by third parties and preserved laboratory samples shall be sealed in such manner that the integrity of the sample can be maintained.

Samples required for (potential) regulatory investigations shall be sealed to a level that meets the requirements of the authorities or other organization(s) concerned with the transport of the sample.

During transportation samples shall be stored in a cooling device capable of maintaining a temperature between (5 ± 3) ^{o}C. For proper evaluation of the conditions during transport a device capable of recording the (maximum) temperature of the air surrounding the sample can be used.

NOTE Devices, capable of logging of the air temperature during the transportation are available but the use and adequate calibration may be costly.

7 Sample reception

Laboratory staff shall receive and check relevant information on preservation and transport conditions of the sample.

All information regarding sample manipulation, handling, and storage shall be included in a sampling report.

In all cases, and especially when a “chain of custody” process needs to be established, the number of sample containers received in the laboratory shall be verified against the number of sample containers submitted.

8 Identification of samples

Container labels should withstand wetting, drying and freezing without detaching or becoming illegible. The labelling system shall be waterproof to allow use in the field.