

Water quality — Sampling —

Part 3: Guidance on the preservation and handling of water samples

The European Standard EN ISO 5667-3:2003 has the status of a
British Standard

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National foreword

This British Standard is the official English language version of EN ISO 5667-3:2003. It is identical with ISO 5667-3:2003. It supersedes BS EN ISO 5667-3:1996/BS 6068-6.3:1996 which is withdrawn.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/6, Sampling, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled “International Standards Correspondence Index”, or by using the “Search” facility of the *BSI Electronic Catalogue* or of British Standards Online.

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Summary of pages

This document comprises a front cover, an inside front cover, the EN ISO title page, the EN ISO foreword page, the ISO title page, pages ii to vi, pages 1 to 31, the Annex ZA page, an inside back cover and a back cover.

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Water quality - Sampling - Part 3: Guidance on the preservation and handling of water samples (ISO 5667-3:2003)

Qualité de l'eau - Échantillonnage - Partie 3: Lignes directrices pour la conservation et la manipulation des échantillons d'eau (ISO 5667-3:2003)

Wasserbeschaffenheit - Probenahme - Teil 3: Anleitung zur Konservierung und Handhabung von Proben (ISO 5667-3:2003)

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Foreword

This document (EN ISO 5667-3:2003) has been prepared by Technical Committee ISO/TC 147 "Water quality" in collaboration with Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2004, and conflicting national standards shall be withdrawn at the latest by June 2004.

This document supersedes EN ISO 5667-3:1995.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of ISO 5667-3:2003 has been approved by CEN as EN ISO 5667-3:2003 without any modifications.

NOTE Normative references to International Standards are listed in annex ZA (normative).

INTERNATIONAL STANDARD

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Water quality — Sampling —

Part 3:

Guidance on the preservation and handling of water samples

Qualité de l'eau — Échantillonnage —

*Partie 3: Lignes directrices pour la conservation et la manipulation des
échantillons d'eau*



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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 (general methods)*.

This third edition cancels and replaces the second edition (ISO 5667-3:1994), 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*
- *Part 2: Guidance on sampling techniques*
- *Part 3: Guidance on the preservation and handling of water samples*
- *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 12: Guidance on sampling of bottom sediments*
- *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 17: Guidance on sampling of suspended sediments*
- *Part 18: Guidance on sampling of groundwater at contaminated sites*
- *Part 19: Guidance on sediment sampling in marine areas*

Introduction

This part of ISO 5667 is intended to be used in conjunction with ISO 5667-1 and ISO 5667-2, which deal with the design of sampling programmes and sampling techniques respectively.

Water quality — Sampling —

Part 3:

Guidance on the preservation and handling of water samples

1 Scope

This part of ISO 5667 gives general guidelines on the precautions to be taken to preserve and transport all water samples including those for biological analyses but not those intended for microbiological analysis.

These guidelines are particularly appropriate when spot or composite samples cannot be analysed on-site and have to be transported to a laboratory for analysis.

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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-14:1998, *Water quality — Sampling — Part 14: Guidance on quality assurance of environmental water sampling and handling*

ISO 5667-16:1998, *Water quality — Sampling — Part 16: Guidance on biotesting of samples*

ISO Guide 34:2000, *General requirements for the competence of reference material procedures*

3 Preservation of samples

3.1 General considerations

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 determinands), the concentrations determined may 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, for example 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 and compounds, of nitrogen, phosphorus and sometimes silicon.
- b) Certain compounds can be oxidized by the 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 $\text{Al}(\text{OH})_3$] or be lost to the vapour phase (for example oxygen, cyanides and mercury).
- d) The pH and conductivity can be modified and the dissolved carbon dioxide changed by the absorption of carbon dioxide from air.
- 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 determinands, to analyse the sample with a minimum of delay.

Preservation of water samples is necessary for a number of reasons, therefore it is generally necessary to choose, from the various possible methods of preservation, a method that does not introduce contamination.

Fresh waters and groundwaters can be stored more successfully. In the case of potable waters, storage can be solved easily by cooling, because these waters are less susceptible to biological and chemical reactions.

In many cases, if samples are analysed within 24 h, the preservation technique of cooling to between 1 °C to 5 °C is sufficient. Municipal or industrial sewage plant effluents should be preserved immediately after sampling, because of the high biological activities in these samples.

This part of ISO 5667 describes the most commonly used preservation techniques and storage times.

In spite of investigations^[4] which have been carried out in order to recommend methods that enable water samples to be stored without changes occurring to their composition, no guidance has been reported that covers all situations. Users of particular test methods and analytical techniques described in International Standards prepared by ISO/TC 147 are encouraged to take into account any relevant guidance offered in this part of ISO 5667 when making decisions in relation to sample preservation and handling for such methods and techniques.

3.2 Precautions to be taken

3.2.1 Container selection

The choice of sample container is of major importance and ISO 5667-2 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 to 4. The same considerations given to this selection of suitable container material should also be given to the selection of cap-liner materials. The guidance given here is to help in the selection of containers for general use.

The containers used to collect and store the samples should be selected after taking into account the following predominant criteria (especially when the analytes are present in trace quantities).

- a) Minimizing sample contamination by the container or cap material, for example leaching of inorganic constituents from glass (especially soda glass) and organic compounds and metals from plastics. Some coloured caps may contain significant levels of heavy metals.
- b) Ability to clean and treat the walls of the container to reduce surface contamination by trace constituents such as heavy metals or radionuclides.
- c) Chemical and biological inertness of the container or cap material in order to prevent or minimize reaction between sample constituents and the container.
- d) Containers may also cause changes to constituent concentrations by adsorption or absorption of analytes. Trace metals are particularly susceptible to these effects but other analytes (for example detergents, pesticides, phosphates) may also be affected.

Guidance should be sought from laboratory staff on the selection of sample containers and sampling equipment.

Other factors should also be considered, e.g. resistance to temperature extremes, resistance to breakage, ease of sealing and reopening, size, shape, mass, availability, cost, potential for cleaning and re-use.

Container blanks should always be taken, preserved and analysed as a check on the suitability of the container and preservation procedures (see ISO 5667-14).

3.2.2 Container preparation

3.2.2.1 General

All preparation procedures should be validated to ensure positive or negative interferences do not occur. As a minimum, this should include the analysis of:

- a) blanks;
- b) samples containing known levels of relevant analytes.

If disposable or single-use containers cannot be used, it is preferable to reserve a set of containers for a particular determinand, thereby minimizing risks of cross-contamination. Care should be taken to prevent a container, formerly holding a sample with a high concentration of a determinand, from contaminating a subsequent sample containing a low concentration of the same determinand.

It may be necessary to wash new containers with water containing a detergent, in order to remove dust and residues of packing materials, followed by thorough rinsing with water of an appropriate quality. The use of cleansing reagents and solvents may cause interferences, e.g. residual contamination by phosphate-containing detergents when undertaking nutrient analyses. If used, all cleaning reagents and solvents should be of an appropriate quality. For the determination of silicon, boron and surfactants, detergents should not be used for cleaning purposes.

3.2.2.2 Detergent-washed plastic or glass containers

The procedure should be as follows.

- a) Wash the container and cap with a dilute solution of detergent and water.
- b) Rinse thoroughly with tap water.
- c) Successively rinse twice with water of an appropriate quality.
- d) Drain thoroughly and replace cap.

Automatic dish washing machines may be used for this procedure.

3.2.2.3 Solvent-washed glass containers

WARNING — Organic solvents may be hazardous. Provide suitable handling facilities and handle with care.

The procedure should be as follows.

- a) Wash the container and cap with a dilute solution of detergent and tap water.
- b) Rinse thoroughly with tap water.
- c) Successively rinse twice with water of an appropriate quality and dry.
- d) Rinse with acetone of an appropriate quality and drain.
- e) Rinse with a suitable solvent of an appropriate quality, dry and immediately replace cap.

The solvent should be compatible with the analytes of interest and the analytical method to be used.

3.2.2.4 Acid-washed containers in plastic or glass

The procedure should be as follows.

- a) Wash the container and cap with a dilute solution of detergent and tap water.
- b) Rinse thoroughly with tap water.
- c) Rinse with an aqueous 10 % nitric acid solution.
- d) Drain and completely fill with an aqueous 10 % nitric acid solution.
- e) Cap and store for at least 24 h.
- f) Empty the container, rinse with water of an appropriate quality and immediately replace cap.

Some manufactures will supply containers with a certificate of cleanliness. Such containers may not need further cleaning or rinsing, provided the manufacturer supplies the containers with caps attached.

Automatic hot acid washers may be used for this procedure.

3.2.3 Filling the container

For samples requiring the determination of physico-chemical determinands, fill the container completely and stopper it in such a way that there is no air space above the sample. This reduces interaction with the gas phase, and minimizes agitation of the sample during transport.

Where samples are frozen as part of their preservation, sample containers should not be completely filled (see 3.2.6).

3.2.4 Handling and preservation of samples for biological examination

The handling of samples for biological examination is different to that for samples requiring chemical analysis. The addition of chemicals to the sample for biological examination can be used for either fixation 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