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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)*.

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This third edition cancels and replaces the second edition (ISO 5667-3:1994), which has been technically revised.

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

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— *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*

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— *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*

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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.

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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

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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.

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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.

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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 $Al(OH)_3$] 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.

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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.

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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).

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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

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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;

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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.

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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.

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c) Rinse with an aqueous 10 % nitric acid solution.

d) Drain and completely fill with an aqueous 10 % nitric acid solution.

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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

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enters the cell quickly. Some preservatives, for instance acid solutions of Lugol, 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. This can be addressed by using an additional preservative, such as alkaline solutions of Lugol, during, for example, the summer period when the appearance of silico-flagellates may be frequently observed.

The preservation of samples for biological examination should meet the following criteria:

a) the effect of the preservative on the loss of the organism should be known beforehand;

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

c) the preservative should enable the taxonomical groups of organisms to be adequately studied during the storage period of the samples.

3.2.5 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.

3.2.6 Cooling or freezing of samples

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The cooling or freezing of samples is only effective if the process is applied immediately after the collection of the samples. This necessitates the use of cool-boxes or refrigerators at the sampling location. Wherever a temperature is given for cooling, the temperature of the sample environment is meant (not the temperature of sample itself).

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Simple cooling of the sample (in melting ice or in a refrigerator at a temperature between 1 °C and 5 °C) and storage of the sample in the dark is, in most cases, sufficient to preserve the sample during transport to the laboratory. Cooling cannot be considered as a means of long-term storage, particularly in the case of wastewater samples (see Table 1). The sample should be kept and stored at a temperature lower than that observed during the process of collection or filling of the container.

A small volume of ice does not have much cooling effect upon a large volume of warm water. Where a sample contains determinands that are likely to be affected by biological activity, and where preservation on-site is not possible, the temperature of the sample should be taken immediately on arrival at the laboratory. This is particularly important when samples require transporting for several hours. Samples should be analysed or cooled immediately at receipt in the laboratory. During transport, the temperature of the cooling system should be monitored.

In general, storage of samples at temperatures below – 20 °C allows the samples to be stored for longer periods of time. If samples are to be frozen, the container should be made of plastic and not be filled completely. This reduces the risk to the sample container from being damaged. For some analytes, such as nutrient determinands, freezing of the sample is the preferred method of preservation. In these cases, quick-freezing with dry ice is a satisfactory procedure. The freezing of samples is not an appropriate procedure for samples requiring analysis of volatile substances or if samples contain cells or bacteria or microalgae, which can fracture and lose cell constituents during the freezing process. Nevertheless, it is necessary to control the freezing and thawing technique in order to return the sample to its initial equilibrium after thawing. In this case, the use of plastic containers (for example polyvinyl chloride or polyethene) is strongly recommended. For thawing of samples, see ISO 5667-16.

3.2.7 Filtration or centrifugation of samples

Suspended matter, sediment, algae and other micro-organisms may be removed, either at the time of taking the sample or immediately afterwards, by filtering the sample through membrane filter material (e.g. paper,

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polytetrafluoroethylene, glass) or by centrifuging. Filtration is, of course, not applicable if the membrane filter is likely to retain one or more of the constituents to be analysed. It is equally essential that the membrane filter assembly system not be a cause of contamination and be carefully washed before use, but in a manner consistent with the final method of analysis.

Alternatively, the reason for filtering the sample may be to enable the proportion of soluble and insoluble forms of an analyte to be determined (e.g. soluble and insoluble metal fractions).

Decanting the sample is not recommended as an alternative to filtration.

Membrane filters should be used with caution as various heavy metal compounds and organic material may be adsorbed on the membrane filter surface, and soluble compounds (e.g. surfactants) within the membrane filter can be leached out into the sample.

3.2.8 Addition of preservatives

Certain physical and chemical constituents can be stabilized by the addition of selective chemical compounds, either directly to the sample after it has been taken, or beforehand, to the empty container.

Particular reagents, necessary for the specific preservation of certain constituents (e.g. the determination of oxygen, total cyanides and sulfides) require the sample to be preserved on-site.

It is essential that the preservatives used do not interfere with the analysis; tests intended to check their compatibility are necessary in case of doubt. Any dilution of the sample with added preservative solutions should be taken into account during the analysis and calculation of results. It is preferable that the addition of preservatives to samples be made using concentrated solutions so that only small volumes are used. In most cases, this enables the corresponding dilution to be disregarded. The use of solid preservatives, for example sodium hydroxide, is to be avoided as local heating may occur, adversely affecting the sample.

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The fact that the addition of these agents can modify or change the chemical or physical nature of the constituents means that these changes are not incompatible with the purpose of later determinations. For example, acidification can solubilize colloidal constituents or solids, and should therefore be used with caution if the aim of the analysis is the determination of dissolved constituents and then only for that purpose. Filtration of the sample prior to the addition of preservative is essential for dissolved ions. Similarly, caution should be applied if the aim of the analysis is to determine the toxicity of the sample to aquatic animals, as certain components, particularly heavy metal compounds, are more toxic in the ionic form. Samples should therefore be analysed as soon as possible.

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It is essential to carry out a blank test, particularly in determinations for trace elements, to take into account the possible introduction of an additional quantity of the determinand (for example acids can introduce a significant amount of arsenic, lead and mercury) by the preservatives. In such cases, samples of the preservatives used for the treatment of the water samples should be retained for use in the preparation of blank tests.

3.3 Reagents

WARNING — Certain preservatives (e.g. acids, alkalis, formaldehyde) need to be used with caution. Sampling personnel should be warned of potential dangers and that 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 should be of at least analytical reagent grade and water should be of at least ISO 3696:1987 Grade 2 purity. Acids referred to in this part of ISO 5667 are the commercially available “concentrated” acids.

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

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