
British Standard

Water quality

Part 6. Sampling

Section 6.3 Guidance on the preservation and handling of samples

[ISO title : Water quality — Sampling — Part 3 : Guidance on the preservation and handling of samples]

Qualité de l'eau

Partie 6. Échantillonnage

Section 6.3 Guide général sur la conservation et la manipulation des échantillons

Wasserqualität

Teil 6. Probenahme

Abschnitt 6.3 Leitfaden für die Aufbewahrung und den Transport von Proben

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National foreword

This Section of this British Standard, which has been prepared under the direction of the Environment and Pollution Standards Committee, is identical with ISO 5667/3-1985 'Water quality – Sampling – Part 3 : Guidance on the preservation and handling of samples'. The international standard was prepared by subcommittee 6, Sampling, of Technical Committee 147, Water quality, of the International Organization for Standardization (ISO) as a result of discussion in which the UK participated.

This British Standard is being published in a series of Parts subdivided into Sections that will generally correspond to particular international standards. Sections are being, or will be, published in Parts 1 to 6 which, together with Part 0, are as follows.

- Part 0. Introduction
- Part 1. Glossary
- Part 2. Physical, chemical and biochemical methods
- Part 3. Radiological methods
- Part 4. Microbiological methods
- Part 5. Biological methods
- Part 6. Sampling

Terminology and conventions. The text of the international standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards; attention is drawn especially to the following.

The comma has been used as a decimal marker. It is

current practice in British Standards to use a full point on the baseline as the decimal marker.

Wherever the words 'part of ISO 5667' appear, referring to this standard, they should be read as 'Section of BS 6068'.

In British Standards it is current practice to use the symbol 'L' for litre (and its submultiples) rather than 'l', and to use the spelling 'sulphur', etc., instead of 'sulfur', etc.

Cross-references

International standard	Corresponding British Standard
ISO 5667/1-1980	BS 6068 Water quality Section 6.1 : 1981 Guidance on the design of sampling programmes (Identical)
ISO 5667/2-1982	Section 6.2 : 1983 Guidance on sampling techniques (Identical)
ISO 6228-1980	BS 6337 General methods of chemical analysis Part 1 : 1983 Method for determination of traces of sulphur compounds by reduction and titrimetry (Identical)

Compliance with a British Standard does not of itself confer immunity from legal obligations.

0 Introduction

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

1 Scope and field of application

This part of ISO 5667 gives general guidelines on the precautions to be taken to preserve and transport water samples.

These guidelines are particularly appropriate when a sample (spot or composite sample) cannot be analysed on site and has to be transported in order to be analysed in the laboratory.

2 References

ISO 5667/2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

ISO 6228, *Chemical products for industrial use — General method for determination of traces of sulphur compounds, as sulphate, by reduction and titrimetry*.

3 Preservation of samples

3.1 General considerations

Waters, particularly surface waters and above all waste waters, are susceptible to being changed to differing extents as a result of physical, chemical or biological reactions which may take place between the time of sampling and the analysis. The nature and rate of these reactions are often such that, if the necessary precautions are not taken before and during transport as well as during the time in which the samples are preserved in the laboratory before being analysed, the concentrations determined will be different from those existing at the time of sampling.

The causes of variations are numerous; some of these are

- Bacteria, algae and other organisms can consume certain constituents present in the samples; they can also modify the nature of the constituents to produce new

constituents. This biological activity affects for example the contents of dissolved oxygen, carbon dioxide, nitrogen compounds, phosphorus and sometimes silicon.

- Certain compounds can be oxidized by the dissolved oxygen contained in the samples or by atmospheric oxygen [for example organic compounds, iron(II), sulfides].
- Certain substances can precipitate out [for example calcium carbonate, metals and metallic compounds such as $\text{Al}(\text{OH})_3$, $\text{Mg}_3(\text{PO}_4)_2$] or be lost to the vapour phase (for example oxygen, cyanides, mercury).
- The pH, conductivity, carbon dioxide content, etc. can be modified by the absorption of carbon dioxide from the air.
- Metals dissolved or in a colloidal state as well as certain organic compounds can be adsorbed or absorbed irreversibly on the surface of containers or solid materials contained in the samples.
- Polymerized products can depolymerize; conversely, simple compounds can polymerize.

The extent of these reactions is a function of 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, the conditions (for example rest or agitation during transport) to which it is submitted, etc.

It follows that the variations relative to a particular constituent vary both in degree and rate, not only as a function of the type of water, but also, for the same type, as a function of seasonal conditions.

It must be emphasized moreover that these variations are often sufficiently rapid so as to modify the sample considerably in the space of several hours. It is therefore essential in all cases to take the necessary precautions to minimize these reactions, and in the case of many parameters to analyse the sample with a minimum of delay.

As the variations which take place in the water samples are due to a large extent to biological processes, it is generally necessary to choose from the various possible methods of preservation a method that does not introduce unacceptable contamination.

Even the time for which the preserved sample can be stored before being analysed may change.

As a guide, it can be said that methods of preservation tend to be less effective in the case of crude sewage than in the case of purified sewage (effluents from biological treatment plants). It has also been observed that the behaviour of various waste water samples during storage is different according to whether the samples have been taken from municipal or industrial sewage-treatment plants.

On the other hand, surface waters and ground waters can in general be stored more effectively. In the case of potable waters, the problem of storage can be solved more easily because these waters are less susceptible to biological and chemical reactions.

Therefore, owing to these variations, which may affect the water samples, it may be necessary, in certain determinations, to take individual samples rather than collective samples and to analyse them immediately at the place of sampling. It should be remembered that the storage of samples for long periods is only possible for the determination of a limited number of parameters.

In spite of numerous investigations which have been carried out in order to recommend methods which will enable water samples to be stored without modification of their composition, it is impossible to give absolute rules in this context which will cover all cases and all situations and which do not have exceptions.

In every case the method of storage shall be compatible with the analytical techniques which will be used. One object of the following is thus to describe the most commonly used techniques.

3.2 Feasible precautions

3.2.1 Filling the container

In the case of samples for the determination of physico-chemical parameters one simple precaution, which is not, however, adequate in all cases, is to **fill the flasks completely and stopper them** in such a way that there is no air above the sample.

This limits interaction with the gas phase and agitation during transport (thus avoiding modifications in carbon dioxide content, and hence variations in pH; hydrogencarbonates are not converted into precipitable carbonates; iron has less tendency to be oxidized, thus limiting colour variations; etc.).

Sample containers, whose contents are frozen as part of their preservation, should not be completely filled.

3.2.2 Use of appropriate containers

The choice and the preparation of a container can be of major importance. ISO 5667/2 gives some guidance on this subject.

However, it should be remembered that the container in which the sample is stored and the stopper should not

- be a cause of contamination (for example borosilicate or soda-lime glass containers may increase the content of silica or sodium)

- absorb or adsorb the constituents to be determined (for example hydrocarbons may be absorbed in a polyethylene container, traces of metals may be adsorbed on the surface of a glass container)
- react with certain constituents in the sample (for example fluorides reacting with glass).

It should be remembered that the use of opaque containers or brown (non-actinic) glass containers can reduce the photo-sensitive activities to a considerable extent.

Blank samples should be taken, preserved and analysed as a check on the suitability of the choice of container and cleaning procedure.

3.2.3 Cleaning of containers

3.2.3.1 For samples for general chemical analysis

For analysis of trace quantities of chemical constituents of surface or waste water, it is usual to clean new containers thoroughly in order to minimize possible contamination of the sample; the type of cleaners used and the container material vary according to the constituents to be analysed.

For general purposes, new glass containers should be cleaned with water and detergents, to remove dust and packing material. They should then be cleaned with chromic acid-sulfuric acid mixture before being thoroughly rinsed with distilled water.

It may be desired, for environmental or health reasons, to avoid the use of chromic acid. Alternatively, proprietary cleaning agents may be used, provided it has been established that they do not cause sample contamination.

It should be noted that detergents possibly containing phosphates cannot be used if phosphates or surface active agents are to be determined, nor can chromic acid-sulfuric acid mixture be used if trace quantities of sulfate and chromium are to be determined.

Polyethylene containers in general should be cleaned by filling with 1 mol/l nitric or hydrochloric acid, leaving for 1 to 2 days followed by thorough rinsing with distilled or deionized water.

3.2.3.2 For samples for determination of pesticides, herbicides and their residues

In general, brown glass containers should be used because plastics, except polytetrafluorethylene (PTFE), may introduce interferents which can be significant if trace analyses are to be performed.

The containers should be cleaned with water and detergent, followed by thorough rinsing with distilled water, then oven dried and cooled before being rinsed with hexane or petroleum ether. Finally they should be dried with a stream of carefully purified air or nitrogen.

A continuous extraction with acetone for 12 h, followed by a hexane rinse and drying as described above, can also be used.

3.2.3.3 For samples for microbiological analysis

The containers shall withstand a 160 °C sterilization and shall not produce or release at this temperature any chemicals which would either inhibit biological activity, induce mortality or encourage growth.

When lower sterilization temperatures are used, polycarbonate and heat resistant polypropylene containers may be used. Caps or other stoppers shall withstand the same sterilization temperatures as the containers.

Glass containers should be cleaned with water and detergent, followed by thorough rinsing with distilled water. Then they should be rinsed with nitric acid (HNO₃) followed by thorough rinsing with distilled water in order to remove heavy metals or chromate residues.

A total of 0,1 ml of a 10 % (m/m) solution of sodium thiosulfate (Na₂S₂O₃) can be added, for every 125 ml of container capacity, before sterilization. This is to eliminate inhibition of bacteria by chlorine.

3.2.4 Cooling or freezing of the samples

The sample should be kept at a temperature lower than that during filling. Containers should be completely filled.

3.2.4.1 Simple cooling (in melting ice or in a refrigerator between 2 and 5 °C) and storage of the sample in the dark are, in most cases, sufficient to preserve the sample during the transport to the laboratory and for a relatively short period of time before the analysis. Cooling cannot be considered as a means of long term storage, particularly in the case of waste water samples.

3.2.4.2 Freezing (– 20 °C) allows in general an increase in the period of storage. Nevertheless, it is necessary to master the freezing and thawing technique fully in order to return the sample to its initial equilibrium after thawing. In this case, the use of plastic containers (for example polyethylene) is strongly recommended.

Glass containers are not suitable for freezing. Samples for microbiological analysis should not be frozen.

3.2.5 Filtration or centrifuging 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 filtration of the samples, through filter paper or membrane filter or by centrifuging. Filtration is, of course, not applicable if the filter is likely to retain one or more of the constituents to be analysed. Equally, the filter must not be a cause of contamination and it must be carefully washed before use.

Alternatively, the reason for analysis may involve the separation of soluble and insoluble forms (for example of a metal) by filtration.

Membranes shall be used with caution as various heavy metals and organic material may be adsorbed on the membrane surface, and soluble compounds within the membrane can be leached out into the sample.

3.2.6 Addition of preservatives

WARNING — The use of mercury(II) chloride (HgCl₂) shall be avoided, unless absolutely necessary, because of its toxicity to the environment. When it has been used, treatment of the residues in order to recover the mercury shall be provided for (see also ISO 6228, annex C).

It should be remembered that certain preservatives [for example acids, mercury(II) chloride, chloroform] must be used with caution, considering the danger involved in their handling. Operators shall be warned of these dangers and the ways of protecting themselves from them.

Certain constituents can be stabilized by the addition of chemical compounds, either directly to the sample after taking it, or beforehand, to the container when it is still empty.

Various chemical compounds, at concentrations equally varied, have been proposed.

Those most commonly used are

- acids
- basic solutions
- biocides
- particular reagents, necessary for the specific preservation of certain constituents [for example the determination of oxygen, total cyanides and sulfides requires a previous fixation of the sample on site (see the corresponding International Standards on analysis)].

It is essential that the preservatives used do not interfere during the determination; tests intended to check their compatibility are necessary in cases of doubt. Any dilution of the sample with added preservatives should be taken into account during the analysis and the calculation of the results.

It is preferable that the addition of preservatives be made using sufficiently concentrated solutions so that only small volumes are necessary. This enables the corresponding dilution to be disregarded in most cases.

The addition of these agents can also modify the chemical or physical nature of the constituents and it is necessary therefore that these modifications are not incompatible with the objects of later determinations. (For example acidification can solubilize colloidal constituents or solids and shall therefore only be used with caution if the aim of the measurements is the determination of dissolved constituents. If the aim of the analysis is to determine the toxicity to aquatic animals, the solubilization of certain components, particularly heavy metals which are toxic in ionic form, has to be avoided. Samples should therefore be analysed as soon as possible.)