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Water quality — Sampling —

Part 9:
Guidance on sampling from marine waters

Qualité de l'eau — Échantillonnage —

Partie 9: Guide pour l'échantillonnage des eaux marines

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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.

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.

International Standard ISO 5667-9 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 6, *Sampling (general methods)*.

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 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*

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— *Part 11: Guidance on sampling of groundwaters*

— *Part 12: Guidance on sampling of sludges and sediments*

Annex A forms an integral part of this part of ISO 5667. Annex B is for information only.

Introduction

This part of ISO 5667 is one of a group of standards dealing with the sampling of specific types of water. It should be read in conjunction with ISO 5667-1, ISO 5667-2 and ISO 5667-3, which deal respectively with the design of sampling programmes, sampling techniques and on the preservation and handling of samples.

Water quality — Sampling —

Part 9:
Guidance on sampling from marine waters

1 Scope

This part of ISO 5667 provides guidance on the principles to be applied to the design of sampling programmes, sampling techniques and the handling and preservation of samples of sea water from tidal waters (for example, estuaries and tidal inlets, coastal regions and the open sea). It does not apply to the collection of samples for microbiological or biological examination. General guidance on sampling for microbiological purposes is given in ISO 8199.

The main objectives of this part of ISO 5667 are specified in 1.1 to 1.4.

1.1 Quality characterization measurement

Measurement of variations in spatial distribution and temporal trends in water quality to establish the effects of climate, biological activity, water movements and the influences of man, and also to assist in determining the magnitude and consequences of future changes.

1.2 Quality control measurement

Measurement of water quality over a long period of time at one or more defined places to establish whether water quality, once characterized, remains suitable for defined uses such as bathing, protection of aquatic life, demineralization or cooling purposes, and to establish whether observed changes are unacceptable.

1.3 Measurements for specific reasons

Assessment of the cause, magnitude and effect of significant variations in water quality and investigation of the sources and subsequent fate of pollutants discharged into marine waters. Identification of pollution, for example invertebrate, fish or bird mortality, or other conspicuous phenomena such as colour or turbidity development, or formation of floating layers of dirt or oil, which can be ascribed to discharges, spillages or even plankton blooms. However, it must be stressed that this objective is often very difficult to achieve. Mortalities may be caused by natural phenomena and cumulative pollutants may often remain largely unseen.

1.4 Examination of the effects of man-made structures

Assessment of water quality variations caused by engineering developments such as barrages, jetties, bridges, breakwaters or ports, and resulting from the extensive use of marine waters for waste disposal.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 5667. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 5667 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 5667-4:1987, *Water quality — Sampling — Part 4: Guidance on sampling from lakes, natural and man-made.*

ISO 6107-2:1989, *Water quality — Vocabulary — Part 2.*

ISO 8199:1988, *Water quality — General guide to the enumeration of micro-organisms by culture.*

3 Definitions

For the purposes of this part of ISO 5667, the following definitions apply.

3.1 spot sample: A discrete sample taken randomly (with regard to time and/or location) from a body of water. [ISO 6107-2]

3.2 depth profile samples: A series of water samples taken from various depths of a body of water at a specific location. [ISO 5667-4]

NOTE 1 In order to obtain a characterization of the water quality throughout the water body it is necessary to take depth profile samples at various locations.

3.3 area profile samples: A series of water samples taken from a particular depth of a body of water at various locations: in tidal waters, either length profiles (along the length of the channel) or cross profiles (across the length of the channel), in coastal waters and the open sea along either a one- or two-dimensional plan-view grid. [ISO 5667-4]

NOTE 2 As in 3.2, characterization may demand a three-dimensional approach to sampling.

3.4 composite samples: Two or more samples or subsamples, mixed together in appropriate known proportions (either discretely or continuously), from which the average result of a desired characteristic may be obtained. The proportions are usually based on time or flow measurements. [ISO 6107-2]

4 Sampling equipment

4.1 Sample container

General guidance is given in ISO 5667-2.

It is essential that special regard be given to the need to prevent contamination or losses through absorption of the low levels of many substances prevalent in sea water, and also to the problems which arise in relation to the high ionic strength of sea water compared to most other natural waters. Glass or other inert materials should be used if there is a risk of interaction of the sample with the container.

NOTE 3 Further details are described by Berman and Yeats (1985)[1].

When sampling at sea, fragile containers should be avoided.

4.2 Types of sampling equipment

4.2.1 Introduction

Subsurface samples can be satisfactorily collected by simple (manual) submersion of the sample container. The top can then be opened, and the container allowed to fill before recapping. It is essential for the bottle to be washed out several times with the water to be sampled before the definitive sample is collected. Plastics gloves should be worn by the operator to avoid contamination of the sample which should be taken upstream or up-tide of the sampling platform and in open water. This can be achieved by taking the sample from a point ahead of the bows of a boat as it moves slowly into the wind or current. This simple method minimizes any possible contamination and prevents possible absorptive losses on the internal surfaces of a sampling device.

The various mechanical aids developed to collect samples from different depths are described in 4.2.2 to 4.2.4.

NOTE 4 Further details are included in "Methods of Seawater Analysis" (1983)[2].

4.2.2 Open samplers and surface samplers

Open samplers are open-mouthed vessels which are used for sampling at, or immediately beneath, the water surface. Open samplers cannot usually be recommended for subsurface sampling because of contamination by the surface layer, which may contain concentrations of some compounds which are sufficiently elevated to influence the overall concentration in the bulk sample.

Samples from the surface microlayer should be taken with samplers specially designed for this purpose, but it is difficult to obtain representative samples, particularly under field conditions.

NOTE 5 The surface microlayer can only really be sampled in a qualitative manner. However, the chemistry of the microlayer and sampling methods have been extensively reviewed by Liss (1975)[3].

4.2.3 Closed-pipe devices

Closed-pipe samplers are hollow tubes fitted with valves or stoppers which are recommended for obtaining samples from defined depths (either spot

samples or a series of samples) or for obtaining depth-integrated composite samples.

Most closed-pipe samplers are made of polyvinylchloride (PVC) or similar material and are, therefore, a ready source of contamination. To avoid this, samplers should be internally coated with polytetrafluoroethylene (PTFE), well-aged and have silicon rubber or PTFE "O" jointing rings. Internal springs made from rubber and external metal springs should be avoided where there is a risk of contamination with the determinands of interest.

Two types of design exist:

— air displacement;

— open ended.

Air-displacement samplers are lowered on a rope, with both orifices closed by stoppers which are attached either to a second line to the surface, or to the main lowering line by non-elastic cords which bypass a spring link in that line. Water pressure and drag limit the depth in which these samplers will operate successfully. Because of this they are most suitable for sampling in estuarine waters, but may be successfully utilized in the surface layers of more open waters.

Open-ended samplers are free-flushing as they are lowered through the water column on a hydrographic cable. It is imperative that a non-metallic rope/hydrographic cable be used if sampling for trace metals or hydrocarbons. The tubes are closed by tightly fitting end caps or shutters triggered electromagnetically, or by messenger weights or water pressure. When in position, the sampler should be allowed 5 min to "acclimatize" to its surroundings before operating. If messenger weights are to be used, they should be plastics coated. Some designs are lowered with shutters closed, preventing contamination with the surface microlayer and water from different layers.

When operating in strong currents or at great depths, the hydrographic cable is unlikely to be vertical. The location of sampling devices in the water column may be established using pressure transducers or echo sounders. In simpler situations, it is sufficient to record the length of wire drawn out and the angle of the wire and to correct to actual depth by using simple geometry.

Samples from close to the seabed should be taken with samplers specially designed for this purpose.

4.2.4 Pumping devices

Peristaltic pumps or centrifugal pumps with impellers which are unlikely to introduce contamination can be used. Sampling tubes are lowered in the water body with the aid of a non-metallic hydrographic cable. The open end of the tube should be kept well away from the cable and the pump and the tube well flushed before the sample is taken. This type of device may be used for taking spot samples or a series of samples from defined depths, or for obtaining depth-integrated or area-integrated composite samples.

Pumping devices may be used to sample chemically stable determinands in both the particulate or dissolved phase, but they are unsuitable for gaseous or volatile compounds.

4.2.5 Automatic sampling equipment

Most automatic sampling devices allow the collection of discrete samples at regular predetermined time intervals. Systems are often combined with on-site monitors, data loggers and telemetry links. Complex automatic monitoring stations have been operated from stationary vessels or fixed monitoring platforms, utilizing *in situ* probes to measure some determinands both at surface and depth. Further details on when these devices may be used are given in 5.3.

5 Sampling procedure

5.1 Sampling location

General guidance on the planning of sampling programmes is given in ISO 5667-1.

The spatial distribution of sampling locations can be decided only after detailed preliminary work using a large number of sampling locations to provide information on which statistical techniques may be applied.

NOTE 6 The wide variety of statistical techniques available is described by Sokal and Rohlf (1969) [4].

The choice of sampling positions is determined by variability in the distribution of parameters of interest, factors influencing that variability and the magnitude of variations which require characterization. It is essential to position individual sampling points in a way that allows credible interpolation between them, otherwise, localized fluctuations will remain undetected or poorly characterized. However, only in special studies of localized fluctuations can one afford to have sampling points close enough to fully reveal patchiness in the chemical constituents of interest.

Unfortunately, it is not possible to give precise guidance because each study would be a unique event.

The practical implications of tidal movement should always be borne in mind. It is important to ensure that sampling at adjacent stations is not carried out

in a way which actually samples the same body of water. This can occur when the inter-station distance is equal to, or less than, the tidal excursion.

Sampling will normally be carried out from the sea using boats, ships, hovercraft or even helicopters. However, when sampling narrow estuaries and tidal creeks it may be more convenient to sample from land using jetties, breakwaters or bridges.

In general, when sampling from moving vessels, it is sufficient to designate sampling points with the aid of navigational position indicators, but these may fail to operate when close to land. Sextants or other navigational instruments can be used to fix position in relation to visible landmarks.

The location of sampling points depends on the area of the marine environment under investigation.

5.1.1 Tidal waters

Water quality in tidal waters is influenced by erosion, river flow, effluent discharges and especially by tidal level and, as a result, the water may be relatively heterogeneous both vertically and horizontally. In order to obtain an accurate picture of the spatial distribution, a preliminary reference frame based on the "mixing" pattern should be determined. This "mixing" pattern can be quantified by measurements of a number of the following parameters: temperature, conductivity (salinity), oxygen concentration, turbidity and/or chlorophyll-fluorescence. For example, longitudinal transects of salinity distribution along an estuary may be made using field instruments, either towed at a fixed depth to measure area profiles or lowered at fixed locations to measure depth profiles. The results of a number of transects can be interpolated in time and space to obtain a tidal average impression of "mixing" pattern.

Subsequent sampling should be directed at the identified heterogeneity, for example, collecting samples at intervals of 2 in salinity [UNESCO (1981) [5]], or more appropriate intervals, for area profile sampling; and collecting samples from the surface, mid-depth and bottom for depth profile sampling.

When investigating the dispersion of an effluent from a specific outfall, the presence of a visible slick may identify the location of the effluent plume at the time of sampling. As an aid to sampling, the trajectory and dispersion of less visible effluents should be labelled, for example using fluorescent dye. However, correlation of the concentration of a dissolved chemical with salinity for samples collected throughout the salinity range is particularly suitable for assessing gain, loss or conservation of the constituent. This can be used to indicate the relative contributions of the chemical from separate discharges.

5.1.2 Coastal regions

Bays, harbours and any other coastal area up to three miles off the coast may belong to this category. Water quality in these areas is again influenced by erosion, river flow and effluent discharges and so may be relatively heterogeneous both vertically and horizontally. Therefore, in order to obtain an accurate picture of the spatial distribution, a preliminary reference frame based on the mixing pattern should be determined. Subsequent sampling should be directed at the identified heterogeneity in either the vertical or lateral plane. The distribution of certain chemical substances, for example nutrients, may be related to factors other than temperature and salinity distribution and require specific investigation.

5.1.3 The open sea

Here the variations in water quality are generally less important than inshore but, at the boundaries of horizontal and vertical currents and upwellings, significant variations can occur. An initial hydrographic survey will determine whether such variations occur. In such locations, salinity, temperature and density profiles should be taken to help to determine the mixing pattern. This will allow samples to be collected from the appropriate layers of discretely different density. It is not recommended to collect excess samples from the same homogeneous layer, except replicates for statistical purposes.

Guidance on statistical considerations is given in ISO 5667-1.

5.2 Frequency and timing of sampling

Cyclic or intermittent fluctuations about average conditions impose temporal variability on the composition of sea water at any fixed location. The frequency of such fluctuations varies from seconds or minutes to years. Significant water quality effects will be associated with long-term seasonal changes such as temperature, precipitation and sunlight and short-term changes such as tidal periodicity (ebb, flow; spring, neap tides) plankton biomass and daylight.

By understanding the physical and biological processes operating in an area (currents, mixing, salinity distribution etc.) it is possible to determine the number of samples required to adequately categorize the water body.

5.2.1 Sampling frequency

5.2.1.1 Sampling frequency for characterization of water quality

Samples for quality characterization should also be collected under non-exceptional conditions and repeated as appropriate to cover the normal range of environmental conditions. Sites should be sampled either at the same time in the tidal cycle, so that valid interpolations between sites can be made, or frequently over the whole tidal cycle. It is essential to complete sampling across a grid rapidly, if a picture of distribution is required for a particular instant in time. Corrections can be applied to the actual sampling positions which allow for tidal movement taking place between the actual times of sampling, or observed concentrations of particular dissolved chemicals can be correlated against salinity.

Full characterization may require an investigation of the combined effects of tidal periodicity, meteorological and climatic conditions. This requires sampling at intervals covering one or more tidal cycles repeated an appropriate number of times throughout the year, to ensure that the results are statistically sound. Detailed guidance is given in ISO 5667-1.

It is essential that investigations around an effluent discharge are designed so that, where the discharge is intermittent, the effects of discharging and not discharging can be fully monitored.

5.2.1.2 Sampling frequency for quality control purposes

Samples for quality control purposes should be collected under non-exceptional conditions with respect to tides, river flow, weather, season, etc. Tidal and coastal waters should be sampled frequently over a tidal cycle, the frequency being dependent on the parameters of interest. Surveys should be repeated to cover the normal range of environmental conditions, with opportunistic sampling of any significant abnormal conditions.

5.2.2 Statistical considerations

Detailed guidance on statistical considerations is given in ISO 5667-1.

Simple statistical evaluations of sampling frequency based on the assumption that the data are independent, randomly sampled and normally distributed can be used with success. However, considerable replication of sampling may be required for the detection of small differences between water samples where the inherent temporal and spatial variability is significant. The design of sampling programmes for rivers and effluents has been discussed by Montgomery and Hart (1974) [6]. Many of their suggestions are applicable to investigations in coastal waters.

Further information is given in 5.1.

5.2.3 Optimization of sampling effort

There will always be a finite limit to the number of samples which can be collected, processed, analysed and reported on, but this limit cannot reduce either temporal or spatial resolution to such an extent that the aims of the investigation are unobtainable. Optimum procedure may entail an irregularity in the spacing of sampling points. Closer spacing should be utilized in the zones of major importance with respect to the distributions and processes under consideration, with wider spacing further away. Knowledge of hydrographic and hydrological conditions will aid optimization of the sampling effort.

5.3 Choice of sampling method

The choice of sampling method depends on the objective of the sampling programme. Samples taken for special reasons or quality control are in most cases spot samples, but tidally induced variability may demand several spot samples. For monitoring water quality, a series of discrete spot samples should be taken, but composite samples may be useful to reduce analytical costs. Composite samples are recommended when an indication of mean values is required. They are not recommended when details of extreme conditions or the extent of quality variation are required. Both methods may be combined by collecting composite samples at short intervals and a full series of samples occasionally.

Sampling at discrete times only yields results which are characteristic of those times. There are times when sampling is not recommended, for example, during periods of high winds when it is dangerous to go to sea. Automatic sampling stations should be considered for monitoring water quality under these extreme conditions, or to investigate the effects of irregular variations in water quality.

5.4 Preservation, stabilization, filtration and storage of samples

ISO 5667-3 gives general guidance on sample preservation and handling.

It is recommended that as many determinations are completed on site as can be managed without impeding or interrupting the sampling programme. Determinands such as temperature, redox-potential and certain others, can only be satisfactorily measured on site.

Sample containers should be tightly sealed and protected from the effects of light or heat. When analysis cannot be completed on board the survey

vessel, storage of samples should be minimized and should not exceed 24 h. Storage should be at 4 °C. Samples should be filtered, stabilized or preserved as necessary, before storing over longer periods of time. Due consideration should be given to the low concentration of impurities and high ionic strength of the samples.

6 Safety precautions

ISO 5667-1 specifies some general safety precautions. Sea conditions can make the use of boats and sampling equipment potentially dangerous. Any risks should be considered and minimized and local safety regulations obeyed. It is essential that the boat is suitable for use in the particular sampling area, and that all boat handlers are fully trained and experienced before being allowed to operate in this potentially hazardous environment.

It is essential to wear appropriate safety equipment at all times.

7 Sample identification and records

A record of the source of the sample and the field conditions under which it was collected should be completed. The record should include the following information:

a) sample location;

b) sampling date and time;

c) sample depth;

d) field data at sample depth (e.g. temperature, salinity, dissolved oxygen, pH, alkalinity, suspended solids);

e) nautical coordinates of site location;

f) description of site location;

g) weather conditions;

h) tidal currents;

i) state of sea during sampling;

j) depth profiles from field instruments;

k) samples collected, determinations required;

l) details of preservation or stabilization.

Each sample bottle should be clearly and indelibly marked with an identification number which is referenced on the sampling record form.

Reference should be made to annex A for an example of a sampling record form.

Annex A
(normative)

Example of a sampling report form for marine waters

Report — Sampling from marine waters

Site: ..... Date: .....
Latitude: ..... Longitude: ..... Time: .....
Description: .....
.....

Hydrographic conditions

Tidal currents: Direction ..... Approx. velocity .....
Time of high water: ..... Time of low water: .....

Weather conditions

Wind: Direction ..... Force .....
Cloud cover: ..... State of sea: .....

Depth (m)	Temperature (°C)	Salinity	Dissolved oxygen (% sat.)		Sample	
					Number	Time

Sampling method: .....
.....

Analysis profiles: .....
.....
.....

Remarks: .....
.....

Sampler: .....

Annex B
(informative)

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