

Nederlandse norm

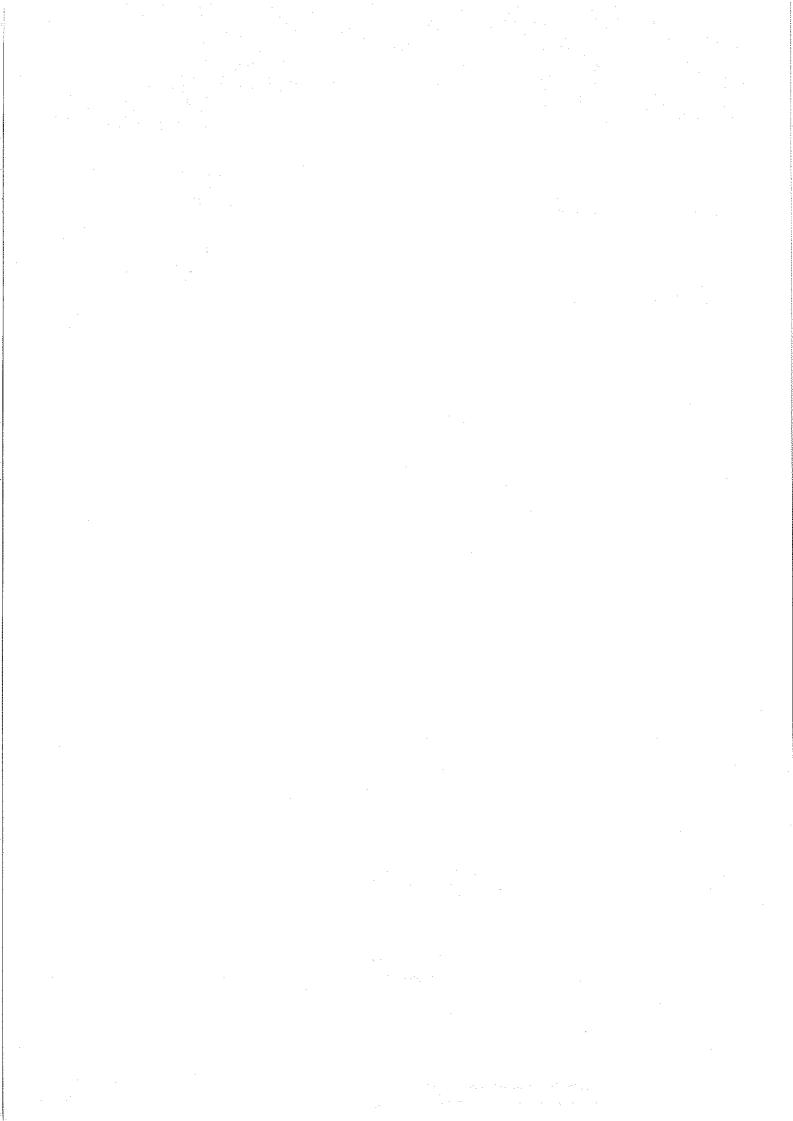
NEN-EN-ISO 5667-1

(en)

Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2006,IDT)

> Vervangt NEN-EN-ISO 5667-1:2005 Ontw.; NEN-ISO 5667-1:1994; NEN-ISO 5667-2:1993

> > ICS 13.060.45 januari 2007



Als Nederlandse norm is aanvaard:

- EN ISO 5667-1:2006,IDT
- ISO 5667-1:2006,IDT

Normcommissie 390 147 "Waterkwaliteit"

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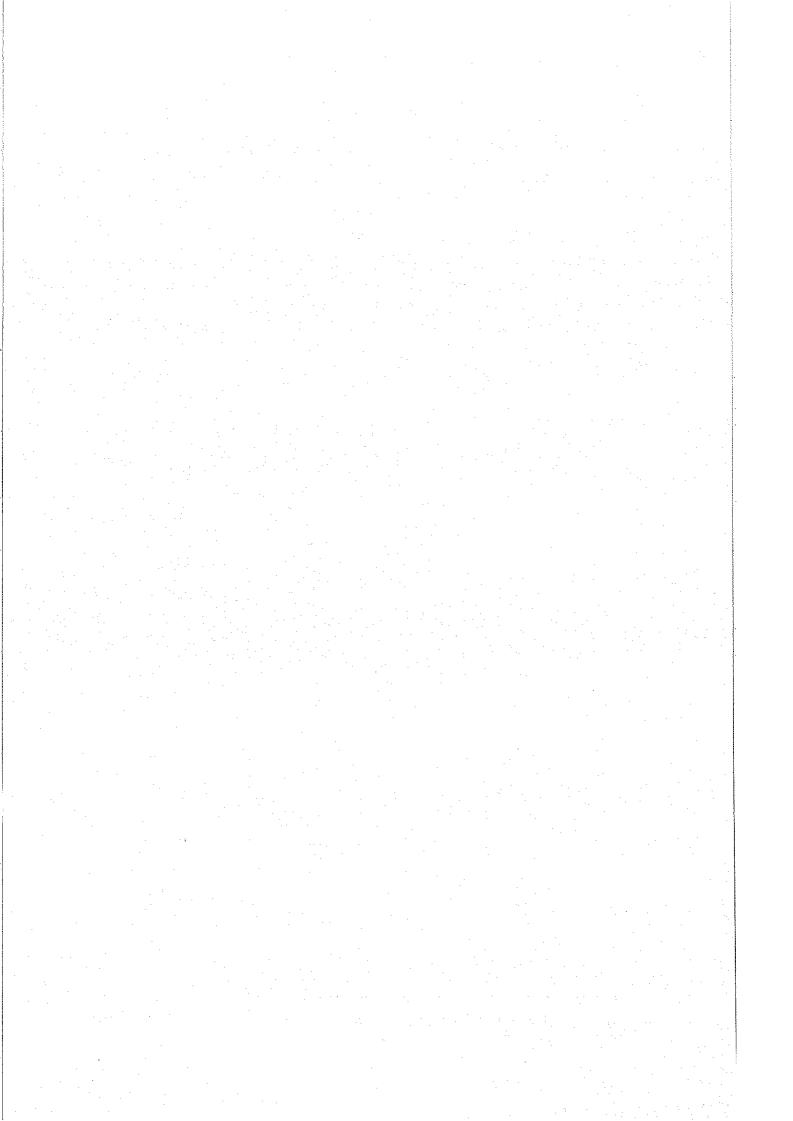
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Nederlands voorwoord

Voor de in deze norm vermelde normatieve verwijzingen bestaan in Nederland de volgende equivalenten:

vermelde norm	Nederlandse norm	titel
ISO 6107-1	-	••
ISO 6107-2	-	_



EUROPEAN STANDARD

NORME EUROPÉENNE EUROPÄISCHE NORM

EN ISO 5667-1

December 2006

ICS 13.060.45

Supersedes EN 25667-1:1993

English Version

Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1:2006)

Qualité de l'eau - Échantillonnage - Partie 1: Lignes directrices pour la conception des programmes et des techniques d'échantillonnage (ISO 5667-1:2006)

Wasserbeschaffenheit - Probenahme - Teil 1: Anleitung zur Erstellung von Probenahmeprogrammen und Probenahmetechniken (ISO 5667-1:2006)

This European Standard was approved by CEN on 25 November 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION COMITÉ EUROPÉEN DE NORMALISATION EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN ISO 5667-1:2006) 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 2007, and conflicting national standards shall be withdrawn at the latest by June 2007.

This document supersedes EN 25667-1:1993.

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

Endorsement notice

The text of ISO 5667-1:2006 has been approved by CEN as EN ISO 5667-1:2006 without any modifications.

INTERNATIONAL STANDARD

ISO 5667-1

Second edition 2006-12-15

Water quality — Sampling —

Part 1:

Guidance on the design of sampling programmes and sampling techniques

Qualité de l'eau — Échantillonnage —

Partie 1: Lignes directrices pour la conception des programmes et des techniques d'échantillonnage



Reference number ISO 5667-1:2006(E)

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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 5667-1 was prepared by Technical Committee ISO/TC 147, Water quality, Subcommittee SC 6, Sampling (general methods), and by Technical Committee CEN/TC 230, Water analysis, in collaboration.

Within ISO, this second edition cancels and replaces the first edition of ISO 5667-1:1980, ISO 5667-1:1980/Cor.1:1996 and the second edition of ISO 5667-2:1991, which have been technically revised. Within CEN, this document supersedes EN 25667-1:1993 and EN 25667-2:1993.

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

- Part 1: Guidance on the design of sampling programmes and 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 from treatment works and piped distribution systems
- 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 sampling of marine sediments
- Part 20: Guidance on the use of sampling data for decision making Compliance with thresholds and classification systems

Water quality — Sampling —

Part 1:

Guidance on the design of sampling programmes and sampling techniques

1 Scope

This part of ISO 5667 sets out the general principles for, and provides guidance on, the design of sampling programmes and sampling techniques for all aspects of sampling of water (including waste waters, sludges, effluents and bottom deposits).

It does not include detailed instructions for specific sampling situations, which are covered in the various other parts of ISO 5667. Also, it does not include microbiological sampling, which is covered in ISO 19458 [23].

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 6107-1, Water quality — Vocabulary — Part 1

ISO 6107-2, Water quality — Vocabulary — Part 2

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6107-1, ISO 6107-2 and the following apply.

3.1

periodic sampling

process of taking samples at fixed intervals which can be time-, volume- or flow-dependent

3.2

area profile sampling

process of taking samples at chosen locations in a specific area while keeping other parameters (e.g. time, depth) as constant as possible

3.3

depth profile sampling

process of taking samples at chosen depths at a specific location while keeping other parameters (e.g. time, flow) as constant as possible

4 General safety precautions

The enormously wide range of conditions encountered in sampling water bodies and bottom deposits can subject sampling personnel to a variety of safety and health risks. Precautions should be taken to avoid inhalation of toxic gases and ingestion of toxic materials through the nose, mouth and skin. Personnel responsible for the design of sampling programmes and for carrying out sampling operations should ensure that sampling personnel are informed of the necessary precautions to be taken in sampling operations.

Attention is drawn to the requirements of national and/or regional health and safety regulations.

NOTE Precautions against accidents might need to be taken. More specific situations are discussed in 5.3.

Weather conditions should be taken into account in order to ensure the safety of personnel and equipment and it is essential that life jackets and lifelines should be worn when sampling large masses of water. Before sampling from ice-covered waters, the location and extent of weak ice should be carefully checked. If self-contained underwater breathing apparatus or other diving equipment is used, it should always be checked and maintained in accordance with relevant ISO or national standards to ensure reliability.

Boats or platforms used for sampling purposes should be capable of being maintained in a stable condition. In all waters, precautions should be taken in relation to commercial ships and fishing vessels; for example, the correct signal flags should be flown to indicate the nature of the work being undertaken.

Sampling from unsafe sites, such as unstable river banks, should be avoided wherever possible. If this is not possible, the operation should be conducted by a team using appropriate precautions rather than by a single operator. Wherever possible, sampling from bridges should be used as a substitute for bank sampling unless bank conditions are the specific subject of the sampling study.

Safe access to sampling sites in all weather is essential for frequent routine sampling. Where relevant, precautions should be taken where additional natural hazards are present, such as fauna or flora, that can endanger the health or safety of personnel.

Hazardous materials (e.g. bottles containing concentrated acids) should be properly labelled.

If instruments or other items of equipment are to be installed on a river bank for sampling purposes, locations that are susceptible to flooding or vandalism should be avoided or appropriate precautions taken.

Many other situations arise during the sampling of water when special precautions should be taken to avoid accidents. For example, some industrial effluents can be corrosive or can contain toxic or flammable materials. The potential dangers associated with contact with sewage should also not be overlooked; these can be gaseous, microbiological, virological or zoological, such as from amoebae or helminthes.

Gas protection equipment, breathing apparatus, resuscitation apparatus and other safety equipment should be available when sampling personnel need to enter sampling locations containing hazardous atmospheres. In addition, the concentration of oxygen and of any likely toxic or asphyxiating vapour or gas likely to be present should be measured before personnel enter enclosed spaces.

In the sampling of steam and hot discharges, special care is necessary, and recognized sampling techniques designed to remove hazards should be applied.

The handling of radioactive samples requires special care, and the special techniques required should be strictly applied.

The use of electrically operated sampling equipment in or near water can present special electrocution hazards. Work procedures, site design and equipment maintenance should be planned so as to minimize these hazards.

5 Design of sampling programmes

5.1 General

Whenever a volume of water, bottom deposit or sludge is to be characterized, it is generally impossible to examine the whole and it is therefore necessary to take samples.

Samples are collected and examined primarily for the following reasons:

- to determine the concentration of associated physical, chemical, biological and radiological parameters in space and time;
- b) with bottom deposits, to obtain a visual indication of their nature;
- c) to estimate the flux of material;
- d) to assess trends over time or over space;
- e) for compliance with, or attainment of, criteria, standards or objectives.

Sampling programmes, the outcome of which will be estimates of summary statistics and trends, should be designed in full awareness of the issues of statistical sampling error and the techniques by which these errors are quantified and how they are used to take decisions.

The samples collected should be as representative as possible of the whole to be characterized, and all precautions should be taken to ensure that, as far as possible, the samples do not undergo any changes in the interval between sampling and analysis (see ISO 5667-3 [3] for additional guidance). The sampling of multiphase systems, such as water containing suspended solids or immiscible organic liquids, can present special problems and in such cases, specific advice should be sought (see Clause 6).

5.2 Broad objectives for the design of sampling programmes

Before any sampling programme is devised, it is very important that the objectives of the programme are carefully established since they are the major factors in determining the position of sampling sites, frequency of sampling, duration of sampling, sampling procedures, subsequent treatment of samples and analytical requirements. The degree of accuracy and precision necessary for the estimation of water quality concentrations sought should also be taken into account, as should the manner in which the results are to be expressed and presented, for example, as concentrations or mass loads, maximum and/or minimum values, arithmetic means, median values, etc. The sampling programme should be designed to be capable of estimating the error in such values as affected by statistical sampling error and errors in chemical analysis.

Additionally, a list of parameters of interest should be compiled and the relevant analytical procedures consulted since these might give guidance on precautions to be observed during sampling and subsequent handling. (General guidance on handling of samples is given in ISO 5667-3 [3].)

It can often be necessary to carry out a preliminary sampling and analysis programme before the final objectives can be defined. It is important to take into account all relevant data from previous programmes at the same or similar locations and other information on local conditions. Previous personal experience of similar programmes or situations can also be very valuable when setting up a new programme for the first time. Putting sufficient effort in time and money into the design of a proper sampling programme is a good investment that will ensure that the required information is obtained both efficiently and economically; failure to put proper effort into this aspect can result in either failure of the programme to achieve its objectives and/or over-expenditure of time and money.

Three broad objectives can be distinguished as follows (these are covered in more detail in 8.2, 8.3 and 8.4):

 quality control measurements within water or waste water treatment plants used to decide when shortterm process corrections are required;

- quality characterization measurements used to estimate quality, perhaps as part of a research project, for setting and measuring performance targets against regulatory targets, for long-term control purposes or to indicate long-term trends;
- identification and control of sources of contamination.

The purpose of the programme can change from quality characterization to quality control and vice-versa. For example, a longer-term programme for nitrate characterization might become a short-term quality control programme requiring increased frequency of sampling as the nitrate concentration approaches a critical value.

No single sampling study can satisfy all possible purposes. It is therefore important that specific sampling programmes are optimized for specific study purposes, such as the following:

- to determine the suitability of water for an intended use and, if necessary, to assess any treatment or control requirements, for example, to examine borehole water for cooling, boiler feed or process purposes or, if a natural spring, as a possible source of water intended for human consumption;
- b) to study the effect of waste discharges, including accidental spillages, on a receiving water;
- c) to assess the performance and control of water, sewage and industrial effluent plants, for example
 - 1) to assess the variations and long-term changes in load entering a treatment works,
 - 2) to determine the efficiency of each stage in a treatment process,
 - 3) to provide evidence of quality of treated water,
 - 4) to control the concentration of treated substances including those which can constitute a health hazard or which can inhibit a bacteriological process, and
 - 5) to control substances which can damage the fabric of plant or equipment;
- d) to study the effects of fresh and saline water flows on estuarine conditions in order to provide information on mixing patterns and associated stratification with variations in tides and freshwater flow;
- e) to identify and quantify products lost from industrial processes; this information is required when product balances across the plant are to be assessed and when effluent discharges are to be measured;
- f) to establish the quality of boiler water, steam condensate and other reclaimed water, enabling its suitability for a particular intended purpose to be assessed;
- g) to control the operation of industrial cooling water systems; this enables the use of water to be optimized and, at the same time, the problems associated with scale formation and corrosion to be minimized;
- to study the effects of atmospheric contaminants on the quality of rainwater; this provides useful information on air quality and also indicates if problems are likely to arise, for example, on exposed electrical contacts;
- i) to assess the effect of inputs from the land on water quality from naturally occurring materials, or contamination by fertilizers, pesticides and chemicals used in agriculture, or both;
- j) to assess the effect of the accumulation and release of substances by bottom deposits on the aquatic biota in the water mass or bottom deposit;
- to study the effect of abstraction, river regulation and river-to-river transfers on natural water-courses; for example, varying proportions of waters of different quality can be involved in river regulation and the quality of the resulting blend can fluctuate;

 to assess changes in water quality which occur in distribution systems for water for human consumption; these changes can occur for a number of reasons, for example, contamination, introduction of water from a new source, biological growths, deposition of scale or dissolution of metal.

On some occasions, the conditions can be sufficiently stable and the forms of variability understood for the required information and the accompanying estimates of errors to be obtained from a simple sampling programme. But, in most locations, quality characteristics are subject to continuous variations in time and space and, ideally, assessment should also be continuous. However, this is often very costly and in many situations impossible to achieve. In the absence of continuous low-error monitoring, and in the use of data collected by sampling, it is vital to take account of statistical sampling error. When considering sampling programmes, the special considerations given in 5.3 should be borne in mind.

5.3 Specific considerations in relation to variability

Sampling programmes can be complex in situations and locations where wide, rapid and continuous variations occur in characteristics such as the concentrations of determinants of interest. These variations can be caused by such factors as extreme changes in temperature, flow patterns or plant operating conditions (as well as in things like chemical analysis). The design of any sampling programme should take this variability into account, either by means of continuous assessment (see Figure A.1) (although this is often very costly and in many situations impossible to achieve), or by taking into account the following recommendations.

- a) The programme should be set in terms of the requirements of techniques that allow the estimation of statistical sampling error.
- Sampling should be avoided at or near boundaries of systems unless those conditions are of special interest.
- c) Care should be taken to eliminate or minimize any changes in the concentration of determinants of interest that might be produced by the sampling process itself, and to ensure that changes during the period between sampling and analysis are avoided or minimized. For detailed guidance on these issues, reference should be made to ISO 5667-14 [14].
- d) Composite sampling may be used to give the best indication of the average composition over a period of time, provided that the determinant being measured is stable during the period of sampling and examination. Data derived from composite sampling should be considered a specific data type in databases so that this type of data is not confused with discrete samples. It should be borne in mind that composite samples are of little value in determining transient peak conditions.

In situations of extreme variability of flow, or concentration, or both (for example, intermittent plant effluents), there may be a benefit in studying the discharge or flow parameters to ascertain whether a pattern is evident, before committing to a particular sampling programme.

5.4 Identifying the sampling location

Depending on the objectives to be achieved (see 5.2), the sampling network can be anything from a single site to, for example, an entire river catchment. A basic river network can comprise sampling sites at the tidal limit, major tributaries at its confluence and major discharges of sewage or industrial effluent.

In designing water quality sampling networks, it is usual to make provision for the measurement of flow at key stations (see Clause 9).

Identifying the sampling location enables comparative samples to be taken. In most river sampling situations, sampling locations can readily be fixed by reference to physical features on the river bank.

On uncovered estuarine and coastal shores, sampling locations can similarly be related to an easily recognizable static object. For sampling from a boat in these situations, instrumental methods for location identification should be used. Map references or other standard forms of reference can be valuable in achieving this.

6 Characteristics and conditions affecting sampling

Flow can change from streamlined to turbulent and vice-versa. Ideally, samples should be taken from turbulent, well-mixed liquids and, whenever possible, turbulence should be induced in flows that are streamlined, except where samples for the determination of dissolved gases and volatile materials are to be collected, the concentration of which can be altered by induced turbulence.

Sampling staff should ensure that "reverse flow", which can occur from other parts of the system, does not produce contamination at the sampling point.

Discrete "slugs" of material can occur at any time, for example, dissolved contaminants, solids, volatile materials or oily surface layers. These should be captured within any sampling programme designed to produce valid and representative samples.

Where sampling from pipes is carried out, the liquids to be sampled should be pumped through pipes of adequate size and at linear velocities high enough to maintain turbulent flow characteristics. Horizontal pipe runs should be avoided. When sampling heterogeneous liquids, pipes with a minimum nominal bore of 25 mm should be used.

When sampling liquids that are corrosive or abrasive, resistance to these conditions should be taken into account. It should be borne in mind that the cheapest course is not necessarily to use expensive chemically-resistant equipment for short-term sampling if the equipment can readily be replaced and contamination of the sample by corrosive products is not likely to be significant.

Sampling programmes should be designed to take into account temperature variation over long or short periods, which can cause changes in the nature of the sample that can affect the effectiveness of equipment used for sampling.

The sampling of waters for suspended solids needs particular care. ISO 5667-17 [16] provides guidance on the sampling of waters for suspended solids, monitoring and investigating freshwater quality and, more particularly, flowing freshwater systems such as rivers and streams. Certain elements of ISO 5667-17 [16] can be applied to freshwater lakes, reservoirs and impoundments; however, field sampling programmes can differ and are not necessarily covered within ISO 5667-17 [16].

Sampling for volatile constituents should be carried out with care. Material being sampled should be pumped with the minimum of suction lift. All pipework should be kept full of the water being sampled and the sample bled from a pressurized pipe after running some of the material to waste to ensure that the sample collected is representative.

The sampling of mixtures of waters of different densities should be carried out with care, for example, layering in a streamlined flow can take place with fresh water over saline water.

The possible presence of toxic liquids or fumes and the possible build-up of explosive vapours should always be taken into account in a sampling situation.

Changes in meteorological conditions can induce marked variations in water quality; such changes should be noted and allowance made for them when interpreting results.

7 Sampling from specific types of water

7.1 Natural waters

The following standards within the ISO 5667 series provide specific guidance on the sampling of a range of natural waters and should be referred to for specific advice.

ISO 5667-6 [6] provides guidance on the sampling from rivers and streams.

ISO 5667-8 [8] provides guidance on the sampling of wet deposition.

ISO 5667-9 [9] provides guidance on the sampling from marine waters.

ISO 5667-19 [18] provides guidance on the sampling of sediments in marine areas.

When sampling from canals, it should be taken into account that the direction of flow can be changeable and the flow rate can vary considerably and be more dependent upon the amount of navigational use (i.e. the number of locking operations) than upon prevailing weather conditions.

It should also be taken into account that stratification and streaming will tend to be more pronounced under the quiescent conditions found in canals than in rivers. The passage of boats can have a very marked shortterm effect on the quality of water in a canal, especially on the suspended solids concentration.

ISO 5667-4 [4] provides guidance on the sampling from natural and man-made lakes.

In naturally formed bathing places, sampling should be carried out as for storage reservoirs and lakes (see ISO 5667-4 ^[4]). In swimming pools with recirculating systems, samples should be taken at the inlet, the outlet and from the body of the water.

ISO 5667-11 [11] provides guidance on the sampling of groundwaters.

ISO 5667-12 [12] provides guidance on the sampling of sedimentary materials from inland rivers, streams, lakes, estuarine and harbour areas.

ISO 5667-17 [16] provides guidance on the sampling of suspended sediments.

ISO 5667-18 [17] provides guidance on the sampling of groundwaters at contaminated sites.

7.2 Processed waters

7.2.1 Industrial water

Processed waters can include water intended for human consumption, river water and borehole water and are usually homogeneous in composition at any given time, although they can vary in quality with time. The water usually enters industrial premises through a conventional system of pipes, and no special sampling situations arise.

If separate, non-potable industrial supplies are available, special care is needed to ensure that the various distribution systems are clearly identified and that there is no uncertainty at the sampling points. To check that a water is suitable for drinking purposes, facilities should be available for sampling. If information on the quality of the final blend of a mixture of waters is required, it is necessary to ensure that adequate mixing has occurred before sampling.

ISO 5667-7 provides guidance on the sampling from boiler plants.

7.2.2 Industrial effluents and process waters

The sampling of industrial effluents has to be considered in relation to the nature and location of each individual effluent.

In general, industrial effluent discharge points can be pipe discharges or open ducts at remote locations where physical access is difficult and no services are available. Alternatively, the discharge points can be readily accessible within the factory premises. It can, on occasion, be necessary to sample from deep manholes and in such cases, specially designed equipment is required. With manhole sampling, it is preferable, for safety reasons, that the manhole should be designed so as to permit sampling to take place without entry.

The possibility of domestic sewage from the factory finding its way into the sample should also be taken into account and the sampling site should therefore be chosen to exclude such wastes, where necessary.

If the effluent discharge is to a lagoon or holding tank, then the sampling situation becomes similar to that for lakes.

In some industrial situations (for example, discharges from individual plant units before further dilution), concentrations of certain constituents can present special difficulties requiring individual attention, such as the presence of oil or grease, high levels of suspended solids, highly acidic effluents and flammable liquids or gases.

When effluents from a variety of processes discharge into a common main, adequate mixing is required in order to obtain a satisfactory sample.

7.2.3 Waste waters and sludges

7.2.3.1 ISO 5667-10 provides guidance on the sampling of waste waters. This can include a wide range of chemical sludges produced in industrial water treatment, such as those containing toxic metals or radioactive materials or biological sludges from effluent treatment plants. When sampling such sludges, suitable safety precautions should be applied. ISO 5667-13 [13] provides guidance on the sampling of industrial sludges derived from water and wastewater treatment.

Samples might be required both when sewage enters a treatment plant and also after various stages of treatment, including samples of the treated effluent.

7.2.3.2 ISO 5667-13 gives guidance on the sampling of sludges from wastewater treatment works, water treatment works and industrial processes. It is applicable to all types of sludges arising from these works and also to sludges of similar characteristics, for example, septic tank sludges. Guidance is also given on the design of sampling programmes and techniques for the collection of samples.

The discharge of such waters normally occurs when flows in the receiving water-courses are high and the dilution available is correspondingly large. For a variety of reasons, however, storm sewage overflows can operate at other times and surface run-off can become contaminated to such an extent that the overflows can represent a serious threat to the quality of a watercourse even under high flow conditions. The sampling of such discharges presents special problems because of their intermittent nature and because the quality can change markedly throughout the period of discharge. The quality is worse in the first flush of the discharge as a result of the initial scouring of sewers and impermeable areas. Automatic sampling devices that collect samples at regular intervals and which start sampling at a prescribed flow offer many advantages but this equipment will need to be installed in a permanent state of readiness. In many instances, the setting of such equipment for flow-dependent sampling will be desirable. The usually highly heterogeneous nature of unmacerated or unsettled storm sewage gives rise to difficulties in obtaining a representative sample and to blocking of equipment. This heterogeneity should be taken into account when sampling techniques and equipment are being selected.

Relevant precipitation and air temperature data should be collected throughout the period of investigation.

7.2.4 Water intended for human consumption and water used in food and beverages

Guidance is provided in ISO 5667-5 [5].

8 Time and frequency of sampling

8.1 General

Information is normally required over a period of time during which the water quality might vary. Samples should therefore be taken at times which will adequately represent the quality and its variations with minimum effort. The sampling programme should be designed to account for seasonal and diurnal cycles and consider

business week cycles, random or transient events, and long-term persistence or trends. This approach contrasts with the choice of sampling frequency based on either subjective considerations or the amount of effort available for sampling and analysis. Both of these methods can lead either to totally inadequate sampling or, in theory, to unnecessarily frequent sampling.

It might be necessary to increase sampling frequency while abnormal conditions persist, for example, during process plant start-up, during flood conditions in a river or at times of algal blooms. In calculating long-term trends, results obtained from these samples should be used only if allowance is made for the increased frequency, and these samples are weighted in time so that a period of intense sampling receives appropriate weight.

8.2 Water quality management programmes

Water quality management programmes usually involve the control of concentration of one or more determinants within defined limits. The results are required in order to decide whether immediate action is needed. The sampling frequency should therefore be chosen to ensure that important deviations outside the control limits are identified between successive measurements. There are two primary factors that fix this frequency:

- a) the magnitude and duration of deviations from the desired conditions;
- b) the probabilities of occurrence of deviations from the desired conditions.

Often, only approximate definitions of these factors will be possible, but reasonable estimates will enable a working value for the sampling frequency to be deduced.

8.3 Quality characterization programmes

Quality characterization programmes aim to estimate one or more statistical parameters that characterize the concentration of one or more determinants or its variability during a defined period, or both. For example, the mean or median indicates the central tendency of results and the standard deviation indicates the variability. The results might be required as part of a research investigation or for characterization of determinants which do not currently need to be controlled or for long-term control purposes.

8.4 Programmes for investigation of causes of contamination

Programmes for investigation of causes of contamination should be designed to determine the characterization of polluting discharges of unknown origin.

They are generally based on a knowledge of the nature or natures of the contaminants, and the coincidence of the periodicity of the appearance of contamination and of sampling.

These criteria necessitate that the sampling, in contrast with that carried out for water quality management and quality characterization, should be carried out with a fairly high frequency in relation to the frequency of appearance of contamination.

Inventory sampling from a large number of locations is often found to be useful in locating undocumented sources of contaminants.

8.5 Statistical considerations

8.5.1 Establishment of sampling programmes

The times and frequencies of sampling in any programme can be properly decided only after detailed preliminary work, in which a high sampling frequency is necessary to provide the information to which statistical techniques may be applied. Once the frequency of sampling has been decided, the data obtained should be reviewed regularly so that changes can be made as required.

If quality is subject to variations, either random or systematic, the values obtained for statistical parameters, such as the arithmetic mean, standard deviation, maximum and percentile values, are only estimates of the true parameters which will generally differ from them. In the case, of purely random variations, the differences between these estimates and the true values can be calculated statistically, and they decrease as the number of samples increases.

The determination of confidence intervals and number of samples using the formula outlined below is an example of the above approach, using one statistical method applied to the arithmetic mean, and assumes that the normal distribution applies to the source data. The terminology used is in accordance with ISO 3534 [2] (all parts) to which reference should be made for definitions of the terms used. For a full treatment of calculation of the mean in terms of confidence interval, reference should be made to ISO 2602 [1].

For more complex calculations involving the assessment of the sampling frequencies, it is necessary to determine other statistical parameters (e.g. percentile values).

For general information on statistical techniques useful for judging the general uncertainty of results of water quality sampling, refer to the *Guide to the expression of uncertainty in measurement (GUM)* [24]

In practice, the confidence interval, L, of the mean of n results, defines the range in which the true mean lies at a given confidence level.

The confidence level is the probability that the true mean will be included within the calculated confidence interval L. A confidence interval for the mean value of a concentration, calculated on the basis of a sample with n results, and at a 95 % confidence level, means that there is a 95 % probability that the interval will contain the true mean (i.e. only a 5 % probability that the true value is outside the interval)

For the case in which a large series of samples are effectively taken, the frequency of cases in which the interval will include the true mean will be close to 95 %.

For a number of results, n, taken at random, estimates of the true mean, μ , and the standard deviation, σ , are the arithmetic mean, \overline{x} , and s respectively according to the following equation:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1}} = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^{n} x_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} x_i \right)^2 \right]}$$

where x_i represents the individual values.

When n is large, s differs little from the true value σ , and the confidence interval of μ calculated from the number of results, n, is $\pm K \sigma / \sqrt{n}$, where K has the value given in Table 1 depending on the confidence level adopted. To estimate the mean for a given confidence interval L at the confidence level chosen, the number of samples necessary is $(2K\sigma/L)^2$. This is strictly true only when σ is known. More samples will be required when only an estimate, s, is available, although this will make little difference to the value of K if s is based on a relatively large number of samples (generally \geq 150). Where estimates are based on less than 30 samples, then, strictly speaking, 'K' should be replaced by Student's t-value (obtainable from tables of the percent points of the t-distribution function).

Table 1 — Values of K

Confidence level (%)	99	98	95	90	80	68	50
K	2,58	2,33	1,96	1,64	1,28	1	0,6

8.5.2 Random and systematic variations of water quality

Random variations commonly have either a normal or a lognormal distribution. Systematic variations may be either trends or cyclic variations, and combinations of the two may occur. The nature of the variability may be different for different determinands in the same water body. If random variations are dominant, times of sampling are generally not statistically important, although they may be important for quality control purposes.

If cyclic variations occur, times of sampling are important if it is necessary to characterize the changes occurring over the whole cycle or to detect maximum or minimum concentrations of interest. Times of sampling should be spaced approximately equally over such periods. In each of the above situations, the number of samples should be governed largely by the statistical considerations outlined above.

In cases where there are cyclic variations (e.g. diurnal or month to month variations) and the objective of a sampling programme is solely to detect whether any systematic changes in quality have occurred between one defined period and another (e.g. over two successive yearly periods), then the most efficient sampling programme is to sample at precisely the same day of the week and time of the day, as this reduces the need to assess quality variations that are not of interest.

In each of the above situations, the number of samples should be governed largely by statistical considerations outlined above. If cyclic variations or systematic variations are either absent or small compared with random fluctuations, the number of samples to be taken need only be large enough to meet the acceptable uncertainty of the statistical parameter being sought at a given confidence level. For example, if normal distribution applies, according to the above, the confidence interval L of the mean of n results, at a chosen confidence level, is given by the equation:

$$L = \frac{2K\sigma}{\sqrt{n}}$$

where σ is the standard deviation of the distribution.

If the required confidence interval were to be 10 % of the mean, the required confidence level 95 % and the standard deviation 20 % of the mean, then

$$10 = \frac{2 \times 1,96 \times 20}{\sqrt{n}}$$

and hence

$$n = 7.84^2$$

and

$$n = 61$$

and hence n is 61 samples.

This indicates a sampling frequency of 2 samples per day if the period of interest were to be 1 month, or of between 1 and 2 samples per week if the period of interest were to be 1 year.

ISO 5667-14 [14] provides guidance on the selection and use of various quality assurance techniques relating to the manual sampling of surface waters, potable waters, waste waters, marine waters and groundwaters.

The general principles outlined in ISO 5667-14 can, in some circumstances, be applicable to sludge and sediment sampling.

8.6 Duration of sampling occasion and composite samples

If only the average quality during a period is of interest, and provided the determination is stable, it can be useful for the duration of collection of samples to be long and preferably done during this period of interest.

This principle is similar to the preparation of composite samples. Both approaches reduce analytical work at the expense of knowledge of quality variations.

9 Flow measurements and situations justifying flow measurements for water quality purposes

9.1 General

The control of sewage and effluent treatment and the quality management of natural waters using mathematical modelling techniques have increased the importance of flow data. For example, contamination loads cannot be assessed without flow measurements. This subclause indicates the flow principles that should be taken into account when setting up a sampling programme. However, as the measurement of flow is not normally made by the water examination scientist, practical details are not included. For these, reference should be made to appropriate International Standards prepared by ISO/TC 30, *Measurement of fluid flow in closed conduits*, and by ISO/TC 113, *Hydrometry*.

There are five aspects of flow that need to be measured, namely,

- a) direction of flow,
- b) velocity of flow,
- c) discharge rate,
- d) flow structure,
- e) cross-sectional area.

9.2 Direction of flow

In most inland watercourses, the direction of flow is self-evident, but in navigational canals and drainage channels this is not always so as the direction of flow can vary with time and there is a possibility of reversal of direction and even counter flow situations. Rivers can also show reverse flow in eddies or in other circumstances.

Knowledge of the pattern of groundwater flow within an aquifer is of primary importance in assessing the consequences of aquifer contamination and in selecting sites for sampling boreholes.

In treatment processes, the pattern of water movement in tanks affects the mixing of the contents, and the settling of suspended matter should be taken into account to ensure that representative samples are collected.

In estuaries and coastal water, it is frequently necessary to measure the direction of water movement as an essential part of the sampling programme. Both direction and velocity can be highly variable, being dependent on tidal currents modified by meteorological conditions and other factors and conditions.

9.3 Velocity of flow

Current velocity is of importance

- a) in calculating the discharge rate,
- in calculating the mean velocity or time of travel which, for water quality purposes, is the time required for a given body of water to move through a given distance,
- in assessing the effect of turbulence and the mixing of a water body produced by velocity.

9.4 Discharge rate

The discharge rate is the volume of liquid that passes a given point per unit time (see Figure A.2). Information on the mean and on extreme rates of discharge is essential for the design and operation of effluent, sewage and water treatment plants, and for setting rational quality limits to safeguard natural watercourses.

9.5 Flow structure

The structure of the flow can strongly influence the rate of mixing vertically and laterally. Care should be taken to assess whether flow is in one confined channel, in several channels (i.e. braided) and whether or not eddies are present. Ideally, samples should be collected from a single, well-mixed channel; observations of flow structure in multiple channels and eddies, for example, suggest that samples might not be representative.

9.6 Cross-sectional area

Sampling cross sections can range from being approximately rectangular to having a deep channel at one edge, from shallow and wide to narrow and deep. These features affect both mixing and erosion, and they can change over time in natural streams and man-made channels.

9.7 Justification for flow measurements in water quality control management

9.7.1 Treatment plant loads

Flow data are necessary in order to assess the polluting load imposed on a treatment plant. This might require making measurements at points of discharge to a sewerage system as well as at the works itself. If the waste water to be treated varies in quantity or quality with time, a continuous-flow discharge record is necessary to obtain a reliable estimate of load. Frequently, composite samples are made up by mixing samples in relation to the recorded flow at the time of sampling. The cost of treatment of trade effluents discharged to public sewers is directly proportional to both the quality and the volume of effluent discharged.

9.7.2 Dilution effects (flux calculations)

Full use of the dilution effects afforded by the receiving sewerage system should be made when evaluating the probable effects of a discharge upon a natural watercourse and the quality limits that need to be imposed on it. The dilution factor should be calculated. While sampling is carried out, the discharge of hazardous substances to public sewers should be controlled so that sampling personnel, sewers and treatment processes are not adversely affected.

9.7.3 Mass flow calculations

Mass flow calculations are widely used in the setting of compliance limits for discharges and for evaluating the quality effects of river abstractions and augmentations. Such calculations are fundamental for modelling quality in whole-river and estuary systems and are frequently based upon typical or mean-flow discharge data. Dynamic modelling techniques require both continuous flow data and computation of flow-frequency values.

9.7.4 Transport of contaminants and rates of recovery

If the concentration of a contaminant in a discharge varies with time, a reliable estimate of the dispersion or degradation of the contaminant can only be obtained if the rate of transport of the contaminant from the point of discharge is known. Hence, a sampling programme for a river or estuary should attempt to sample the same body of water as it moves along the water-course.

When an accidental spillage of a contaminant enters a water-course, a knowledge of the time required for the contaminant to reach downstream abstractors is invaluable in assessing the effects of such contamination.

9.7.5 Flow-related determinants

The concentrations of certain water quality determinants, such as temporary hardness or chloride, have been found, in certain circumstances, to be related to the flow rate in rivers and streams, usually over a limited range. If suitable records are available, linking flow rates with the concentrations, an estimate of water quality in relation to these determinants can be made from flow rate measurements alone. Checks should be made at intervals to ascertain whether the relationships remain valid.

9.7.6 Groundwaters

A reliable assessment of contamination risks to groundwater sources and the expected rates of recovery from them requires a knowledge of the direction and velocity of groundwater movement. This information can then be used to avoid the difficulty and cost of sampling groundwaters for the assessment of contamination.

9.8 Methods available for flow measurement

- **9.8.1** Measurements can be either discrete, such as those made by use of floats in an estuary or a direct-reading current-meter in a river, or they can be continuous, such as those made by most discharge flow meters.
- **9.8.2** Direction and velocity can be measured by using
- a) drogues,
- b) floats and drifters.
- c) chemical tracers (including dyes),
- d) microbiological tracers,
- e) radioactive tracers.
- 9.8.3 Velocity can also be measured by using
- a) current meters, direct-reading and recording types,
- b) ultrasonic techniques,
- c) electromagnetic techniques,
- d) pneumatic techniques.
- 9.8.4 Discharge can be determined by using
- a) velocity measurements made in a channel of known cross-sectional area,
- b) direct mechanical means, such as a tipping bucket or a standard water-meter;

- measurement of water level above a constriction in the flow, such as a weir or flume; the level can be measured
 - 1) visually by means of a gauging board,
 - automatically, by means of a float, changes in electrical resistance, pressure differential, photographically or acoustically;
- d) the following means in a closed pipe:
 - 1) pressure differences across a venturi throat,
 - 2) pressure differences across an orifice plate,
 - 3) pumping rate, multiplied by the duration of pumping,
 - 4) electromagnetic, ultrasonic and other techniques;
 - 5) dilution gauging, for carrying out spot measurement of discharges in natural watercourses.

10 Sampling techniques

10.1 General

There are many sampling situations, some of which can be satisfied by taking simple spot samples, whereas others might require sophisticated instrumental sampling equipment.

The various types of sampling are all examined in some detail in ISO 5667-4 [4] and subsequent parts of ISO 5667, and reference should be made to these whenever required.

Analytical data might be required to indicate the quality of water by determination of parameters such as the concentrations of inorganic material, dissolved minerals or chemicals, dissolved gases, dissolved organic material and matter suspended in the water or bottom sediments at a specific time and location or over some specific time interval at a particular location.

Certain parameters, such as the concentration of dissolved gases, should be measured *in situ* if possible, to obtain accurate results. Sample preservation procedures should be carried out in appropriate cases – see ISO 5667-3 [3] for guidance.

Separate samples should be used for chemical, microbiological and biological analyses because the procedures and equipment for collection and handling are different and are incompatible.

The sampling techniques will vary according to the specific situation. The different types of sampling and associated sampling programmes are described in Clause 7.

It is necessary to differentiate between sampling from standing and flowing waters. Spot samples (10.2) and composite samples (10.6) are applicable to both standing and flowing waters. Periodic sampling (10.3) and continuous sampling (10.4) are applicable to flowing waters, whereas series sampling (10.5) is more applicable to standing waters.

10.2 Spot samples

Spot samples are discrete samples, usually collected manually but which can also be collected automatically, for waters at the surface, at specific depths and at the bottom.

Each sample will normally be representative of the water quality only at the time and place at which it is taken. Automatic sampling is equivalent to a series of such samples taken on a preselected time or flow-interval basis.

Spot samples are recommended if the flow of the water to be sampled is not uniform, if the values of the parameters of interest are not constant and if the use of a composite sample would obscure differences of interest between individual samples due to either masking short-term variations or even reaction between them.

Spot samples should also be carried out, where possible, in investigations of the possible existence of contamination, or in surveys to indicate its extent or, in the case of automatic discrete sample collection, to determine the time of day when contaminants are present. They can also be taken for guidance in the establishment of a more extensive sampling programme. Spot samples are essential when the objective of a sampling programme is to estimate whether a water quality complies with limits not related to average quality. Spot samples should be taken for the determination of unstable parameters, such as the concentration of dissolved gases, residual chlorine and soluble sulfides.

10.3 Periodic samples (discontinuous)

10.3.1 Periodic samples taken at fixed time-intervals (time-dependent)

These samples are taken using a timing mechanism to initiate and terminate the collection of water during a specific time-related interval (see Figure A.3). A common procedure is to pump the sample into one or more containers for a fixed period, a set volume being delivered to each container.

NOTE The parameter of interest can affect the time interval.

10.3.2 Periodic samples taken at fixed flow-intervals (volume-dependent)

These samples can be taken when variations in water quality criteria and effluent flow rate are not interrelated. For each unit volume of liquid flow, a controlled sample can be taken irrespective of time (see Figure A.4).

10.3.3 Periodic samples taken at fixed flow-intervals (flow-dependent)

These samples are taken when variations in water quality and effluent flow rate are not interrelated. At constant time intervals, samples of different volumes are taken, the volume depending upon the flow (see Figure A.5).

10.4 Continuous samples

10.4.1 Continuous samples taken at fixed flow rates (time-continuous samples)

Samples can be taken by this technique at fixed sample flow rates (see Figure A.6) and contain all constituents present during a sampling period, but in many cases, do not provide information about the variation of concentrations of specific parameters during the sampling period.

10.4.2 Continuous samples taken at variable flow rates (flow-continuous samples)

Samples can also be taken at variable sample flow rates in proportion to the flow of water being sampled (see Figure A.7). In this case, the flow-proportional samples collected are representative of the bulk water quality. If both the flow and composition vary, flow-proportional samples can reveal variations that might not be observed by the use of spot samples, provided that the samples remain discrete and a sufficient number of samples is taken to differentiate between the changes in composition. Consequently, this is the most precise method of sampling flowing water if both the flow rate and the concentration of contaminants of interest vary significantly.

10.5 Series sampling

Series sampling can involve a number of samples taken from various depths of a body of water at a specific location (depth profile samples), or a series of water samples taken from a particular depth of a body of water at various locations (area profile samples).

10.6 Composite samples

Composite samples can be obtained manually or automatically, irrespective of the type of sampling (flow-, time- or volume-dependent). Continuously taken samples can be put together to obtain composite samples. Composite samples provide average compositional data. Consequently, before combining samples it should be verified that such data are desired, or that the parameter(s) of interest do(es) not vary significantly during the sampling period. Composite samples are valuable in cases when compliance with a limit is based on the average water quality.

10.7 Large-volume samples

Some methods of analysis for certain determinants require the sampling of a large volume of water, ranging from 50 l to several cubic metres. Such large samples are necessary, for example, when analysing for pesticides or microorganisms that cannot be cultured. The sample can either be collected in a conventional manner, with great care being taken to ensure cleanliness of the container or tanker holding the sample, or by passing a metered volume through an absorbent cartridge or filter, depending on the determinant. For example, an ion exchange cartridge or an activated carbon cartridge can be used to sample some pesticides.

The precise details of the latter procedure depend on the type of water sampled and the determinants. A regulator valve to control the flow through the cartridge or filter should be used for supplies under pressure. For most determinants, a pump should be placed after both the filter or cartridge and the meter. If the determinant is volatile, the pump should be placed as close as possible to the sample origin, with the meter being placed after the filter or cartridge.

When sampling a turbid water containing suspended solids that could blind the filter or cartridge, or if the amount of determinant required for analysis exceeds the capacity of the largest filter or cartridge available, a series of filters or cartridges arranged in parallel should be used, with the inlet and exit manifolds fitted with stopcocks. Initially, the sampling flow should be directed through one filter or cartridge, with the others not receiving the flow, and when the flow rate decreases significantly then the flow should be diverted to a fresh filter or cartridge. If there is a danger of the filter or cartridge being overloaded, then fresh filters or cartridges should be connected on-line sequentially before the original one is exhausted; the flow to the exhausted cartridge is then stopped.

When more than one filter or cartridge is used, they should be treated together and considered as a composite sample. If the waste water from such a sampling regime is returned to the body of water being sampled, then it is essential that it be returned sufficiently distant from the sampling point, so that it cannot influence the water being sampled.

11 Sampling equipment

11.1 General

Reference should be made to ISO 5667-3 [3] for specific sampling situations; the guidelines given here are to assist in the selection of materials for general application. The chemical constituents (determinants) in water, which are analysed to evaluate the water quality, range in concentration from sub-microgram quantities or trace quantities to gross quantities. The most frequently encountered problems consist of adsorption of chemical determinants onto the walls of the sampler or sample container, contamination prior to sampling caused by improper cleaning of the sampler or sample container, and contamination of the sample by the material constituting the sampler or sample container.

The sample container should be designed to preserve the composition of the sample from losses due to adsorption and volatilization, or from contamination by foreign substances.

The sample container used to collect and store the sample should be chosen after considering, for example, resistance to temperature extremes, resistance to breakage, ease of good sealing and reopening, size, shape, mass, availability, cost, potential for cleaning and re-use, etc.

It is recommended that detailed advice be sought from the analyst on the final choice of sample container and sampling equipment.

Precautions should be taken to prevent samples freezing, particularly when glass sample containers are used. High-density polyethylene is recommended as a container material for determinations of silica, sodium, total alkalinity, chloride, specific conductance, pH and hardness determinations in water. For light-sensitive materials, light-absorbent glass should be used. Stainless steel should be considered for taking samples of water under high temperature and/or pressure, or when sampling for trace concentrations of organic material.

Glass bottles are generally (but not always) suitable for organic chemical compounds and biological species, and plastics containers for radionuclides. It is important to note, however, that the sampling equipment of these materials often have neoprene¹⁾ gaskets and oil-lubricated valves. Such materials are not satisfactory for samples for organic and microbiological analysis.

In addition to the desired physical characteristics described above, the sample containers used to collect and store the samples should be selected by taking into account the following predominant criteria (especially when the constituents to be analysed are present in trace quantities):

- a) minimization of contamination of the water sample by the material of which the container or its stopper is made, for example, leaching of inorganic constituents from glass (especially soft glass) and organic compounds and metals from plastics and elastomers (plasticized vinyl cap liners, neoprene jackets);
- b) ability to clean and treat the walls of the containers, to reduce surface contamination by trace constituents such as heavy metals or radionuclides;
- c) chemical and biological inertness of the material of which the container is made, in order to prevent or minimize reaction between constituents of the sample and the container;
- d) sample containers which can also cause errors by adsorption of chemical determinants. Trace metals are particularly liable to this effect, but other determinants (e.g. detergents, pesticides, phosphate) can also be subject to error.

Sampling pipes are generally used in automatic sampling to supply samples to continuous analysers or monitors. During the residence time within the pipe, the sample can be considered as being stored in a container having the composition of the sampling line. Guidelines for the selection of materials for sample containers also, therefore, apply to sampling pipes.

11.2 Types of sample container

11.2.1 General

Polyethylene and borosilicate glass bottles are suitable for conventional sampling for the determination of physical and chemical parameters of natural waters. Other more chemically inert materials, e.g. polytetrafluoroethylene (PTFE), are preferred, but these are often too expensive for routine use. Screw-cap, narrow-mouthed and wide-mouthed bottles should be fitted with inert plastics stoppers/caps or ground glass stoppers (although these are susceptible to seizing with alkaline solutions).

¹⁾ Neoprene is the trade name of the DuPont Company for a family of polychloroprenes. This information is given for the convenience of users of this part of ISO 5667 and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Chemically active filler material should not be used between the bottle cap and liner since such fillers can be a source of contamination.

If the samples are transported in a case to a laboratory for analysis, the lid of the case should be constructed to prevent loosening of the stopper, which could result in spilling and/or contamination of the sample.

To ensure appropriate sample containers are used, refer to ISO 5667-3 [3].

11.2.2 Sample containers for photosensitive materials

In addition to the considerations already mentioned, the storage of samples containing photosensitive materials, including algae, requires their protection from exposure to light. In such cases, containers constructed of opaque materials or non-actinic glass should be used, and they should be placed in light-proof cases during extended periods of storage.

11.2.3 Sample containers for dissolved gases or constituents

For the collection and analysis of samples containing dissolved gases or constituents that would be altered by aeration, narrow-mouthed biochemical oxygen demand (BOD) bottles should be used. These should be fitted with pointed glass stoppers to minimize air occlusion, and thus require special provision for sealing during transportation.

11.2.4 Sample containers for trace organic contaminants

Sample bottles used for trace organic contaminants should be made of glass, as virtually all plastics containers interfere with the highly sensitive analysis. The closure should be of glass or PTFE.

11.2.5 Sample containers for microbiological examination

Guidance on sample containers for microbiological examination is detailed in ISO 5667-16 [15] and ISO 19458 [23]. Sample containers should be able to withstand the high temperatures that occur during sterilization. During sterilization or sample storage, the materials should not produce or release chemicals that could inhibit microbiological viability, release toxic chemicals or encourage growth. The samples should remain sealed until opened in the laboratory, and should be covered to prevent contamination.

12 Sampling equipment for physical or chemical characteristics

12.1 General

The volume of sample collected should be sufficient for the required analyses and for any repeat analyses. The use of very small sample volumes can cause the samples collected to be unrepresentative. In addition, small samples can also increase problems of adsorption because of the relatively high area to volume ratio.

Effective sampling equipment should

- a) minimize the contact time between the sample and the sample container,
- b) use materials such that no sample contamination occurs,
- be simply designed to ensure ease of cleaning, with smooth surfaces and the absence of flow disturbances such as bends and with as few taps and valves as possible (all samplers should be checked to ensure that no bias is being introduced),
- d) be designed with the suitability of the system in relation to the required water sample (i.e. chemical, biological or microbiological) in mind.

For sampling of dissolved gases, reference should be made to 12.5.

12.2 Equipment for spot sampling

Spot samples are usually taken manually according to the conditions described in 10.2. The simplest equipment for taking surface samples is a bucket or wide-mouthed bottle dropped into a body of water and hauled out after filling. The nature of the problem being studied should determine the type of sample that needs to be collected. In general, it is best to take the sample directly into the sample container.

In practice, a weighted bottle is stoppered and lowered into the body of water. At a preselected depth, the stopper is removed and the bottle is then filled and subsequently withdrawn. The effects of air or other gases on the integrity of the sample as it is filled or withdrawn should be taken into account as these can change the parameter being examined (e.g. dissolved oxygen). Special sampling bottles that avoid this problem (e.g. evacuated bottles) are available. For stratified water bodies, a graduated glass, plastics or stainless steel cylinder, open at both ends, can be lowered to obtain a vertical profile of the water body. At the sampling point, the cylinder is stoppered at both ends by a mechanism before withdrawal to the surface. This equipment is often termed a messenger-operated water bottle.

12.3 Grabs or dredges for sampling sediment

Sediments can be sampled by grabs or dredges designed to penetrate the substrate as a result of their own mass or leverage. Design features vary and include spring-activated or gravity-activated modes of jaw closure. They also vary in the shape of the substrate bite, from square to sharp angle, and in the area and size of sample taken. The nature of the sample obtained is therefore affected by such factors as

- a) the depth of penetration of the substrate,
- b) the angle of jaw closure,
- c) the efficiency of closure (ability to avoid obstruction by objects),
- d) the creation of a "shock" wave and resultant loss or "wash-out" of constituents or organisms at the mudwater interface,
- e) the stability of samples in rapidly moving streams.

In selecting dredges, the habitat, water movement, area of sample and any boat equipment necessary should be taken into account.

Clam-shell buckets resemble similar equipment used in land excavation. Usually operated from a boom, they are lowered at a selected sampling site to obtain a relatively massive composite sample. The resulting sample is more precisely defined with respect to a sampling site than when a dredge is used.

12.4 Core samplers

Core samplers are used when information concerning the vertical profile of a sediment is of interest. Unless the sample obtained has mechanical strength, care should be exercised in its removal from the coring device to preserve its longitudinal integrity.

12.5 Sampling equipment for dissolved gases and volatile materials

Samples suitable for accurate determinations of dissolved gases should only be obtained with equipment that collects a sample by displacement of water, rather than air, from the sampler.

If pumping systems are used for the collection of dissolved gas samples, it is essential that the water be pumped in such a way that the pressure applied to it does not drop significantly below atmospheric pressure. The sample should be pumped directly into the storage or analysis bottle, which should be flushed by an amount equal to at least 3 times its volume before starting analysis or stoppering the bottle.

If approximate results are acceptable, samples for dissolved oxygen determinations can be collected using a bottle or a bucket. The error introduced into these determinations by contact between the sample and the air varies with the degree of saturation of the gas in the water.

Where samples are collected in a bottle from a tap or pump outlet, a flexible inert tube that delivers liquid to the bottom of the bottle should be used, to ensure that liquid is displaced from the bottom of the bottle in order to prevent aeration.

Collection of samples for dissolved oxygen from ice-covered water bodies should be conducted with great care to prevent contamination of the samples by air.

12.6 Sampling equipment for radioactivity characteristics

Detailed guidance on sampling radionuclides is contained in ISO 5667-3 [3].

Depending on the objective and the national legal regulations, most of the sampling techniques and equipment available for sampling waters and waste waters for chemical constituents are generally applicable for obtaining samples for the measurement of radioactivity.

The samples should be collected in plastic bottles previously cleaned with detergent and rinsed with water and dilute nitric acid.

12.7 Sampling equipment for biological and microbiological characteristics

Detailed guidance on microbial sampling for water quality is contained in ISO 19458 [23].

Detailed guidance on biotesting of samples is contained in ISO 5667-16 [15].

Detailed guidance on handnet sampling of aquatic benthic macro-invertebrates is contained in ISO 7828 [19].

Detailed guidance on the design and use of quantitative samplers for benthic macro-invertebrates on stony substrata in shallow freshwaters is contained in ISO 8265 [20].

Detailed guidance on the use of colonization, qualitative and quantitative sampling in deep waters for macro-invertebrates is contained in ISO 9391 [21].

Detailed guidance for quantitative sampling and sampling processing of marine soft-bottom macrofauna are contained in ISO 16665 [22].

12.8 Automatic sampling equipment

Automatic sampling equipment can be used to advantage in many sampling situations, since it allows a continuous sample or series of samples to be collected without manual intervention. It is particularly useful in preparing composite samples and studying variations in quality with time.

The choice of the most suitable type of machine will depend on the particular sampling situation, for example, sampling in order to estimate the average load of dissolved trace metals in a river or stream might best be carried out using a continuous flow-proportional device, utilising a peristaltic pumping system.

Automatic sampling devices may be of the discrete or continuous type and may be operated on a time or flow-proportional basis.

Sampling lines are generally used in automatic sampling. Therefore, the guidance on selection of materials for sample containers also applies to sampling lines. The machines operate by pumping river water into sample containers held in the body of the machine and use a variety of pumping systems. The choice of machine depends upon the particular sampling situation. Simple automatic machines may be programmed to take samples at pre-set time intervals or be operated by an external trigger such as a signal generated by excessive rainfall. Many of the time-interval machines are built to take 24 samples and are designed to take

one sample every hour over a 24 h period. The set times are, however, often continuously variable so that all 24 samples may be taken during other time periods. Typical settings could be to cover an 8 h working day, i.e. one sample every 20 min, or one complete week, i.e. a sample every 7 h. If a measurement of flow is available, a manual flow proportional sample may be prepared by blending suitable aliquots from the timed samples.

More refined, flow-proportional machines continuously measure the flow in the river or stream and take samples after a fixed volume of water has passed the sampling point.

Care should be taken to ensure the sample is non-degradable or is suitably stabilized if the sample is to remain in the machine for any length of time.

The sample storage compartment should be cooled to, and maintained at, as low a temperature as possible without the sample becoming frozen so as to reduce any general deterioration of the sample. If, however, the temperature can be expected to fall below freezing, heating will be required. If the determinant of interest is known to deteriorate, specific preservatives should be placed in the sample containers (see ISO 5667-3). The discharge of the sample into the container should be sufficient to mix the preservative into the sample. There will be occasions when mutually exclusive determinants and preservatives are required and, in such cases, more than one sampling machine should be deployed. Used in this mode, the sample containers are filled in a very short space of time, e.g. 1 min to 2 min, which is approaching a "discrete" sample.

If each sample is being analysed, care should be taken to ensure the volume in each container is sufficient for the analysis of interest.

It is essential that the automatic sampling machine itself, or the storage of the samples within it, causes no significant deterioration of the sample that would cause the sample to be unrepresentative. The sample line from the sample point to the machine should not contaminate the sample. For example, copper pipe work should not be used if metal analysis is to be performed. It is always preferable to use inert materials such as PTFE or stainless steel. This also applies to any filter that might be fitted to the inlet. In order to prevent solids settling out, an adequate flow needs to be maintained in the inlet pipe and a constant internal diameter of more than 9 mm is recommended. Automatic sampling machines should have the ability to flush out any residual sample in the sample line. Any associated dead volume should be kept to a minimum. The machine should be maintained and cleaned regularly and it is essential that the sample line is cleaned out at the same frequency as the rest of the sampling equipment to prevent the build up of bacteria etc. Some newer automatic sampling machines are "self-emptying" samplers. Bottles, lines and dosing systems are flushed with clean water at every bottle change. Samples that are not needed for the tests will be automatically emptied, allowing the sampler to run continuously without need for constant operator intervention.

In all cases, the sampling machine should be tested to ensure satisfactory performance in the situation being investigated.

12.9 Preparation of sampling equipment

Sampling equipment should be prepared as shown in Table 2.

Table 2 — Preparations for sampling

Equipment	Preparation			
Sampling vessels	Check for scratches, signs of wear and tear and insecure fitting.			
Funnels				
Ropes				
Chains				
Extension handles				
Filters and filter equipment				
Crates and sample carriers	Check that sufficient numbers are available for daily use. Inspect for damage or signs of deterioration. If necessary, swab the crates with a disinfectant.			
Preservatives	Check that the "use by date" is not exceeded. Check dropper pipette for deterioration and replace as necessary. Ensure segregation from empty sample bottles.			
Bottles	Check the condition of the bottles and caps and discard any damaged ones found so that other sampling operatives do not select them. Ensure bottles are capped to reduce contamination and that they are stored securely. Ensure bottles for microbiology work have either their original wrapping intact or sterility indicator stripes visible and that the bottles are within date.			
Field instruments	Check that calibration is within date. If not, do not use but replace. Follow sampling procedure/manufacturer's instructions for storage.			
Test kits	Check that test kits needed for daily schedule are available for use. Ensure manufacturer's instructions or work instructions are available for use. Check that the "use by date" has not expired; replace if necessary. Store separately from sample bottles.			
Labels and sample documents	If labels are pre-printed, check against schedule to ensure that none are missing.			
Personal safety equipment	Ensure that there are sufficient disposable gloves for the day, mobile phone, ice anchors, first-aid kit, hand wipes, goggles, etc.			
Ice auger	Check the motor starts and the bit is sharp.			

13 Avoidance of contamination

13.1 General

Avoiding contamination during sampling is essential. All possible sources of contamination should be taken into account and the appropriate control applied if necessary.

13.2 Sources of contamination

Potential sources of contamination can include the following:

- a) the residue of earlier samples remaining on sampling containers, funnels, scoops, spatulas and other equipment;
- b) contamination from the sampling site during sampling;
- c) residual water in or on ropes, chains or extension handles;
- d) contamination of funnels from preserved samples;
- e) contamination of bottle caps or tops by dust or water;

- f) contamination of the barrel of syringes and from filter medium;
- g) contamination from hands, fingers, gloves and general handling;
- h) contamination from internal combustion exhaust;
- i) inappropriate sampling devices, bottles and filtration devices;
- j) degraded reagents.

13.3 Control of contamination

Control and identification of contamination can be achieved by the following actions, where appropriate:

- a) adopting a philosophy of maximizing the degree of isolation for the sample bottle from contamination, which produces better quality data;
- b) taking care to avoid disturbance at the sampling site;
- c) thoroughly rinsing the equipment;
- d) rinsing the funnel inside and out after sub-sampling preserved samples;
- e) rinsing the barrel of the syringe and filter medium before use;
- f) storing bottle caps and tops securely to avoid contamination;
- g) wiping and drying ropes, chains or extension handles between sampling and prior to storage;
- h) avoiding touching the sample itself with fingers, hands or gloves; this is particularly important during microbiology sampling where no contact should be made with the interior or rim of the bottle or the cap;
- i) ensuring that all ice augers, vehicles and boats are well downwind (and downstream in the case of boats), allowing a few minutes for exhaust gases to dissipate;
- j) examining each sample or sample bottle for large particles such as leaves or detritus; if these are observed, discard the sample and collect a new sample;
- k) using suitable quality assurance techniques as outlined in ISO 5667-14 [14].

14 Transport to, and storage of samples at, the depot or laboratory

If the samples are to be exposed to excessive heat, i.e. contained in the sampling vehicle in hot conditions, then the samples (or those sub-samples prone to heat degradation) should be cooled. The vehicle should preferably be fitted with a refrigerator (cool boxes can be used but they are not efficient and effectively are only suitable for preventing temperature rise). It should be noted that the BOD of a sample can be reduced by 40 % if stored under high ambient temperatures or light conditions in a sampling vehicle for 8 h.

Samples that cannot be delivered to the laboratory within a day should be stabilized or preserved in accordance with the provisions of ISO 5667-3 [3] or with alternative suitable preservation techniques as agreed with the laboratory. It is the laboratory's responsibility to ensure storage is suitable after the samples have been delivered.

A system should be in operation that clearly identifies to the laboratory courier which samples and associated paper work are for transmission to the laboratory.

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Samples are often stored in the depot in a refrigerator (up to 24 h) or freezer. On thawing, frozen samples often precipitate and can result in erroneous results, particularly for pesticides and polychlorinated biphenyl compounds. If analysis of any of these compounds is required, then freezing should not be employed.

All preservation steps should be recorded in the report and the temperature measured and recorded on site, if appropriate. Ideally other physical and chemical parameters (e.g. pH value) should be determined on site or as soon as possible afterwards.

15 Sample identification and records

15.1 General

The source of the sample and the conditions under which it was collected should be recorded and a suitable record attached to the bottle immediately after filling. A water analysis is of limited value if it is unaccompanied by detailed information about the sample.

The results of any on-site analyses carried out should also be included in a report with the sample. Labels and forms should always be completed at the time of sample collection. The sampler should never move on to another task before completing all documentation at a site.

The sampling report should include at the least the following information:

- a) location and name of sampling site, with coordinates and any other relevant locational information;
- b) details of sampling point, including kind of sample (e.g. water intended for human consumption, waste water).
- c) date of collection;
- d) time of collection;
- e) name of sample collector;
- f) sample type (e.g. single sample, composite sample);
- g) weather conditions;
- h) field observations;
- i) water temperature;
- j) nature of any pretreatment including preservation;
- method of collection and any details of non-compliance with standard conditions or sampling practices (e.g. sample collected through ice, seasonal observations, land-based activities).

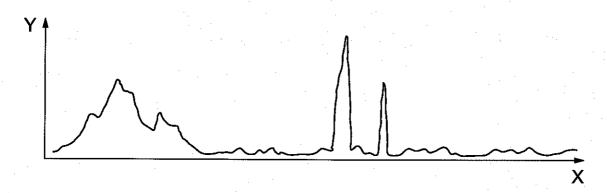
15.2 Samples that might be used for legal purposes

Often a legally defined chain of custody is required which proves who was responsible for the safe keeping of the sample at all times between the moment the sample was taken and the completion of the analysis. The legal system in a particular state will define the requirements that a chain of custody has to fulfil. This will normally include some documentation additional to that normally used for non-legal samples, showing by signature, dates and time who was responsible for the samples. The chain of custody should include the sampling operative, the person delivering the sample to the depot, if different, the laboratory courier and verification that all parts of the sample that were sent have been received.

The courier should deliver the sample to a nominated, responsible officer at the laboratory who should complete the record, and the original copy of the document should be returned to the sampling officer with a copy retained by the laboratory. Alternatively, if the samples are delivered outside normal office hours, some proof that the sample is deposited securely at the depot should be requested.

Annex A (informative)

Diagrams illustrating types of periodic and continuous samples

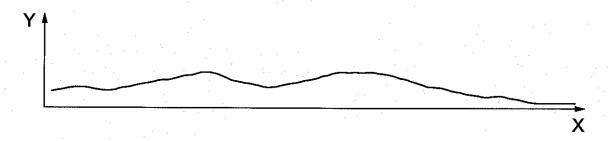


Key

X time

Y concentration

Figure A.1 — Continuous direct measurement — Continuous on-line measurement

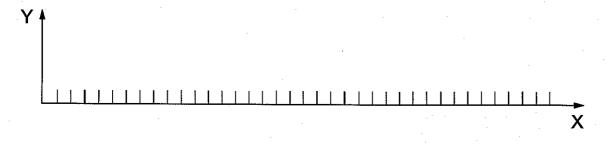


Key

X flow

Y time

Figure A.2 — Periodic samples — Time scale of flow

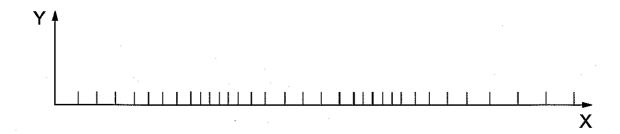


Key

X time

Y volume

Figure A.3 — Periodic samples — Periodic samples taken at fixed time-intervals (time-dependent)

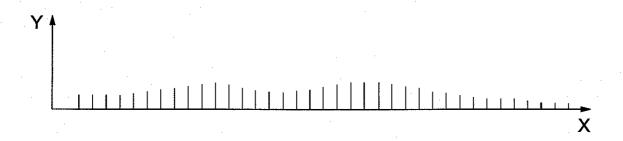


Key

X time

Y volume

Figure A.4 — Periodic samples — Periodic samples taken at fixed flow-intervals (volume-dependent)

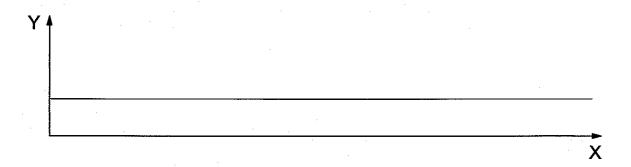


Key

X time

Y volume

Figure A.5 — Periodic samples — Periodic samples taken at fixed flow-intervals (flow-dependent)

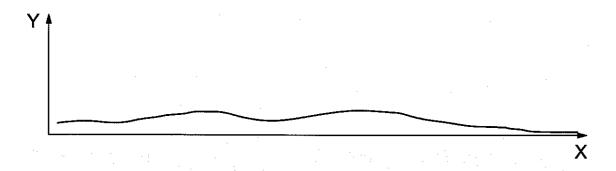


Key

X time

Y volume

Figure A.6 — Continuous samples — Continuous samples taken at fixed flow rates (time-continuous)



Key

X = time

Y = volume

Figure A.7 — Continuous samples — Continuous samples taken at variable flow rates (flow-continuous)

Bibliography

- [1] ISO 2602, Statistical interpretation of test results Estimation of the mean Confidence interval
- [2] ISO 3534 (all parts), Statistics Vocabulary and symbols
- [3] ISO 5667-3, Water quality Sampling Part 3: Guidance on the preservation and handling of samples
- [4] ISO 5667-4, Water quality Sampling Part 4: Guidance on sampling from lakes natural and manmade
- [5] ISO 5667-5, Water quality Sampling Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems
- [6] ISO 5667-6, Water quality Sampling Part 6: Guidance on sampling of rivers and streams
- [7] ISO 5667-7, Water quality Sampling Part 7: Guidance on sampling of water and steam in boiler plants
- [8] ISO 5667-8, Water quality Sampling Part 8: Guidance on the sampling of wet deposition
- [9] ISO 5667-9, Water quality Sampling Part 9: Guidance on sampling from marine waters
- [10] ISO 5667-10, Water quality Sampling Part 10: Guidance on sampling of waste waters
- [11] ISO 5667-11, Water quality Sampling Part 11: Guidance on the sampling of groundwaters
- [12] ISO 5667-12, Water quality Sampling Part 12: Guidance on sampling of bottom sediments
- [13] ISO 5667-13, Water quality Sampling Part 13: Guidance on sampling of sludges from sewage and water treatment works
- [14] ISO 5667-14, Water quality Sampling Part 14: Guidance on quality assurance of environmental water sampling and handling
- [15] ISO 5667-16, Water quality Sampling Part 16: Guidance on biotesting of samples
- [16] ISO 5667-17, Water quality Sampling Part 17: Guidance on sampling of suspended sediments
- [17] ISO 5667-18, Water quality Sampling Part 18: Guidance on sampling of groundwater at contaminated sites
- [18] ISO 5667-19, Water quality Sampling Part 19: Guidance on sampling of marine sediments
- [19] ISO 7828, Water quality Methods of biological sampling Guidance on handnet sampling of aquatic benthic macro-invertebrates
- [20] ISO 8265, Water quality Design and use of quantitative samplers for benthic macro-invertebrates on stony substrata in shallow freshwaters
- [21] ISO 9391, Water quality Sampling in deep waters for macro-invertebrates Guidelines on the use of colonization, qualitative and quantitative samplers
- [22] ISO 16665, Water quality Guidelines for quantitative sampling and sample processing of marine soft-bottom macrofauna

NEN-EN-ISO 5667-1:2007

ISO 5667-1:2006(E)

- [23] ISO 19458, Water quality Sampling for microbiological analysis
- [24] Guide to the expression of uncertainty in measurement (GUM), BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML, 1993²⁾

²⁾ Corrected and reprinted in 1995.

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