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Water quality — Sampling —

Part 10: Guidance on sampling of waste water

Qualité de l'eau — Échantillonnage —

Partie 10: Lignes directrices pour l'échantillonnage des eaux résiduaires

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, SC 6, *Sampling (general methods)*.

This second edition cancels and replaces the first edition (ISO 5667-10:1992), which has been technically revised. The main changes compared to the previous edition are as follows:

— integration of radioactive liquid effluent sampling and its specificities;

— integration of qualified spot sampling.

A list of all parts in the ISO 5667 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Water quality — Sampling —

Part 10:
Guidance on sampling of waste water

1 Scope

This document contains details on the sampling of domestic and industrial waste water, i.e. the design of sampling programmes and techniques for the collection of samples. It covers waste water in all its forms, i.e. industrial waste water, radioactive waste water, cooling water, raw and treated domestic waste water.

It deals with various sampling techniques used and the rules to be applied so as to ensure the samples are representative.

Sampling of accidental spillages is not included, although the methods described in certain cases may also be applicable to spillages.

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

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-7, *Water quality — Sampling — Part 7: Guidance on sampling of water and steam in boiler plants*

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

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

ISO 6107 (all parts), *Water quality — Vocabulary*

ISO 19458, *Water quality — Sampling for microbiological analysis*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6107 (all parts) and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
composite sample
two or more samples or sub-samples, mixed together in appropriately known proportions (either discretely or continuously), from which the average value of a desired characteristic may be obtained

Note 1 to entry: The number of samples or sub samples are usually based on time, flow measurements, area or depth profile sampling.

EXAMPLE Composite sample can be made in different ways:

— constant volume variable time sampling (C.V.V.T): flow proportional sampling based on collecting equal volumes of sample at frequencies proportional to flow.

— constant time variable volume sampling (C.T.V.V): flow proportional sampling based on collecting samples at fixed time intervals but where the volume of sample is varied in proportion to the flow.

— constant time constant volume sampling (C.T.C.V): equal volumes of sample or sub-sample collected at equal increments of time.

3.2
sampling point
precise position within a sampling location from which samples are taken

3.3
spot sample
discrete sample taken randomly (with regard to time and/or location) from a body of water, usually taken manually, but may be taken by automatic sampling equipment or by event-triggered automatic samplers

3.4
qualified spot sample
special form of a *composite sample* (3.1), consisting of at least five spot samples, taken and mixed within a maximum period of two hours and at an interval of not less than two minutes

3.5
radioactive liquid effluent
water or waste water that contains radioactive substances, resulting from a process and that can be recycled, treated and/or discharged to the environment

Note 1 to entry: The activity concentration of the radioactive liquid effluent is usually measured before being discharged in the environment to verify that it is lower than the authorized levels in order to comply with national regulation.

3.6
supernatant
solid or liquid phase present on the surface of an effluent

3.7
planned discharge
discharge subject to prior agreement further to a consultation between several parties based on knowing certain predefined parameters and referring to limit values (regulatory or otherwise)

Note 1 to entry: These parameters may, for example, be physical, chemical and radiological measurements, the estimated discharge volume, the discharge period or the maximum discharge flow rate.

3.8
permanent discharge
direct discharge into a channel or collector or water body, which is not subject to a specific prior agreement, but which shall conform with limit values

3.9
tank
hollow object, very variable in size, used to hold liquids

Note 1 to entry: Covers the usual names such as tank, chamber and pool. The content of this tank is intended for direct and indirect liquid discharge to the environment or to a specific treatment.

3.10
event-trigged sampling
sampling which is triggered because a pre-determined criterion has been met (e.g. rainfall, change in electrical conductivity, pH or the introduction of a polluting substance), when samples should be taken manually or by automatic equipment

4 General aspects

4.1 Design of sampling programme

Sampling is usually the first step in carrying out an investigation and largely determines the quality of the whole investigation. It is therefore recommended that a detailed sampling strategy be drawn up, often based upon a preliminary investigation in which an assessment has identified the important aspects. Both the purpose and the ambient situation determine the way in which the sampling is carried out. General aspects for sampling programme design can be found in ISO 5667-1.

4.2 Sampling point selection - Representativeness

The sampling point selection should be representative of the waste stream to be examined. In some waste waters this representativeness may be difficult to obtain because of the spatial and temporal heterogeneity of the water body. It is necessary to carry out the sampling in the sections where the flow is well mixed and homogeneous.

The term “representativeness” encompasses two notions depending on the type of environment to be sampled:

— representativeness in a flow (canal, sewer, manhole, pressurised pipes, etc.);

— representativeness in a storage (tank, lagoons, basins, etc.).

These two notions should be treated in different ways, but the goal remains to obtain a representative sample of the water body.

Sampling points may be clearly identified (by regulatory text) or not, in which case a preliminary investigation is recommended. This is generally the case for the selection of sewer sampling locations. By studying drawings of the sewer system initially, possible locations can be identified. Subsequently, a site inspection should be conducted to ensure that the locations of the sewers and the path of the waste stream corresponds to the drawings, and to make sure that the selected location is representative for the sampling purpose. The tracer studies may be a helpful tool.

Each sampling point should be documented. It is important to gather, for example, the following information: identification, location of the site, photos, geographical coordinates, site location, type of flow (open, closed), access conditions and sampling technique.

If necessary, specifically describe and label the sampling site. Select the site so that representative samples can be obtained and the waste water flow (with the exception of fixed sampling equipment) is clearly visible from the sampling site.

The following facilities should be available for the for the sampling sites involving a fixed automatic sampling device:

— access for motor vehicles to the immediate vicinity of the sampling site;

— flat working surfaces at appropriate height above the sampling point for the set-up of sampling devices;

— adequate lighting and power connection;

— water connection to clean the equipment after sampling;

— adequate safety precautions (e.g. grids, railings, fall arresting devices); and

— flow meters in the case of a flow-dependent sampling.

If the hydraulic conditions do not ensure the representativeness of the sample (absence of flow, reduced activity, abnormal load rise), this unusual situation should be noted on the sampling report and the client and the analytical laboratory should be informed.

4.3 Frequency and time of sampling

4.3.1 Number of samples

Analyses should be based on samples taken at regular intervals during a certain period (composite or spot). The decision on the required number of samples taken during each period should be decided based on statistical techniques (see ISO 2602,[1] ISO 3534 (all parts)[2] and ISO 5667-1). But the number of samples to be taken may often be decided by the regulatory body or pollution control authorities.

4.3.2 Sampling time for effluent stream

The objective of a sampling programme often dictates when and how a sample is collected and is often determined by legislation or directives. Generally, when sampling sewages and effluents, it is normal to make allowances for the following sources of variation in quality:

a) diurnal variations (i.e. within-day variability);

b) variations between days of the week;

c) variations between weeks and months;

d) variations between seasons;

e) variations due to storm water episodes; and

f) trends.

If there is little or no diurnal variation, or day-to-day variations, then the particular time of day or day of the week for sampling is relatively unimportant.

If the identification of the nature and magnitude of peak load are important, sampling should be restricted to those periods of the day, week or month when peak loads are known to occur.

Relating the times of sampling to the particular process being monitored may be very important when considering industrial effluent discharges that are either seasonal or operated on a batch basis. In either case, the discharge will not be continuous, and the sampling programme will need to take this fact into account.

Sampling for the detection of trends needs careful planning. For example, when detecting trends on a month-to-month basis, it can be appropriate to always sample on the same day of the week, in order that any diurnal and daily variations are eliminated from the overall variability of data, thus allowing trends to be more efficiently detected.

When the number of samples has been decided upon according to 4.3.1, the sampling times should be determined. The samples should normally be taken at fixed intervals during the whole control period. The sampling period may be one year, a number of months or weeks, or even shorter periods of time.

If the sampling period covers one year, the days of sampling may be determined using a formula. An example of this is:

Formula (1) for a number of samples (*n*), larger than about 25 and from Formula (2) for a number of samples less than about 25.

Formula (1) indicates the day number during which sampling should take place.

$$A+\frac{365}{n},A+\frac{365\times 2}{n},A+\frac{365\times 3}{n},\ldots,A+\frac{365\times n}{n} \quad (1)$$

where

n is the number of samples;

A is a random number in the interval between $-\frac{365}{n}$ and 0.

Formula (2) indicates the week number during which the sampling should take place. The day of each week should be determined so that samples are taken on every weekday.

$$B+\frac{52}{n},B+\frac{52\times 2}{n},B+\frac{52\times 3}{n},\ldots,B+\frac{52\times n}{n} \quad (2)$$

where

n is the number of samples;

B is a random number in the interval between $-\frac{52}{n}$ and 0.

Similar formulae can be used for other periods, for example, one month, three months, six months, etc. The period chosen should cover any seasonal variations.

After determining the intervals and the day or week number, it should be ensured that the sampling does not lead to any risk of systematic error, for example by always taking samples on one day, or by systematically omitting weekdays.

5 Sampling at specific locations

The concentration profiles of dissolved substances and suspended solids measured in an effluent are often heterogeneous because they depend on the hydraulic conditions and transport conditions of the solid phase in the body of water. Observations are:

— A vertical gradient of concentration, due to the flow velocities or the shear stresses near the bottom are low;

— A very dense layer at the interface between the deposit of the bottom and the water circulating in the structure;

— An increase of the concentration near the walls;

— An increase of the concentration near the surface of the flow due to the presence of floating matter.

It is therefore necessary to define carefully the positioning of the sample taken within the body of water. To take a sample theoretically representative of the average concentration of the measured section, it is advisable to place the sampling point about halfway up the water column and at a sufficient distance from the walls and deposits to avoid measurement bias.

5.1 Sampling from sewers, channels and manholes

A location should be chosen where the effluent has a high turbulent flow to ensure good mixing. Often accessibility, lack of site security, or power unavailability may preclude the use of the best sites.

Since effluent channels are generally designed to cope with both effluent and storm-water discharge conditions and/or for higher flows than those actually occurring, laminar flow may often occur. In the absence of a location with turbulent flow conditions at permanent sampling location, such conditions should be induced by restricting the flow, for example with a baffle or weir. The restriction should be made in such a way that sedimentation upstream of the restriction does not occur (e.g. foresee enlargement of the downstream effluent channel compared to the upstream channel, to avoid any pressure increase of the effluent downstream).

The sampling intake point should always be located downstream from the restriction and, as a general rule, it should be located at least three times the pipe diameter, or width of the channel, downstream of the restriction. The inlet of the sampling probe should preferably face the direction of flow but may face downstream if too many blockages result.

The exact location of the sampling point should be evaluated with respect to variations in water level, types and concentrations of the determinands, etc. The sampling point should be at a minimum distance from the bottom and walls to avoid sample contamination by deposits or the biofilms that develop. Generally, a sampling point between one third and one half of the effluent water depth below the surface of the water may be recommended.

Whenever practicable, permanent sampling locations should be established, care being taken to ensure reproducible sampling conditions.

Before proceeding with the sampling of industrial discharges and if the information is accessible, the conditions inside the plant (e.g. processes and production rates) should be noted and recorded along with any potential hazards.

5.2 Sampling from waste water treatments plants

When choosing sampling locations for waste water treatment plants, it is again important to refer to the objective of the data collection programme, of which the sampling is a part.

Typical objectives are:

— control of the performance of the entire treatment plant: samples should be collected at the main inlet and main outlet points;

— control of the operation of individual processing units, or groups of units: samples should be collected at the inlet and outlet of the units in question.

When sampling at the waste water treatments plants, the importance, the relevance of any bypass flow should be evaluated, and sampling of such flows may also be needed for the sampling to be representative for the overall effluent.

When sampling at the inlets of plants, the objective of the sampling programme should be carefully considered. In some situations, there may be a need to sample raw sewage in the mixture with recirculated processing liquid (e.g. in the assessment of primary sedimentation tank loadings and efficiency). In other cases, it may be necessary to exclude the effect of these liquids (e.g. when collecting data designed to assess domestic/industrial loadings to a plant or to assist in industrial effluent control).

Representative sampling is often facilitated by using locations downstream of a measuring flume or weir (see also 5.1).

When sampling effluents from processes employing more than one individual treatment unit (e.g. several sedimentation tanks), care should be exercised in ensuring that the sample is representative of the overall effluent stream rather than any one specific treatment unit (unless that unit forms the basis of a specific study).

Frequent reviews of a plant's sampling locations need to be made to ensure that any relevant changes in the operation of unit processes are considered when sampling. For example, the percolating filter operation may be changed from a "single-pass" operation to a "recirculation" or "alternating-double filtration" operation. Treatment plant operation may involve changes in the manner in which feed or return liquors are introduced to the plant (e.g. return of sewage from storm tanks, changes in the position at which processing liquors are returned to the treatment plant).

Whenever sampling waste waters, great care should be exercised to overcome or minimize the substantial heterogeneity caused by suspended solids that are often present. Similarly, thermal stratification of separate industrial effluent streams may be found when sampling effluents or discharges from industrial processes, and measures have to be taken to promote the mixing of such streams before sampling.

5.3 Sampling from industrial sites

Sampling liquid effluents involves sampling a certain representative amount before and/or after they are transferred to discharge channels or collectors.

The sampling method depends on the type of discharge or transfer taking place. The following should therefore be distinguished:

— planned discharges, which require a preceding inspection before the discharge takes place. These may be, for example, discharges from facilities' liquid effluent tanks prior to their transfer to general collectors or buffer pools before being discharged into the environment (refer to 7.4);

— permanent discharges, which concern effluents that are continuously discharged. They are monitored based on sequential or continuous sampling of the discharged effluent. These may be, for example, discharges from an effluent collector at the outlet of a nuclear site or a rainwater collector, prior to discharge into the environment.

As such, the kind of sampling and the creation of representative samples shall be adapted to suit the type of discharge and its potential heterogeneity (e.g. the presence of suspended matter or any density or thermal stratification).

For this, and to guarantee the representative nature, the samples shall be produced:

— ensuring sampling only takes place after obtaining suitable effluent homogeneity;

— ensuring there is no change to the nature of the effluent or cross-contamination; and

— taking account of the volumes of the tanks, the flow rates and the flow conditions in the lines, to enable quantification of the discharges from the facility in question (see Annex A, Figure A.1 for an example of tank sampling).

Sampling may be performed based on several configurations, depending on the facilities:

— in a tank prior to its discharge (see Annex A, Figures A.1 and A.3);

— in a continuous or discontinuous flow in a line or a discharge channel (see Annex A, Figure A.1).

5.4 Sampling from cooling systems

The selection of sampling points in industrial cooling processes using water as a coolant depends on the cooling water system to be tested.

In continuous-flow cooling systems, fresh water (ground water, bank filtrate, surface water) or saline water are used in one or repeated flow. The sampling points are located both in front and behind the aggregates, which shall be cooled.

During cooling via primary and/or secondary circuit, two cooling circuits are coupled to one another, wherein a closed secondary circuit is re-cooled with a primary circuit. The primary circuit can consist of a continuous cooling system, an open or closed recooling plant or a refrigerating plant (e.g. brine cooling). The sampling site should be on the return side and on a well through-flow site of the circulatory system.

In many cases, the cooling water is precooled in an open system by evaporation cooling, whereby water losses due to evaporation, spraying and desludging (desalination) will be replaced by fresh water. In the closed recooling process, the cooling water flows through pipes, which are cooled from outside by air or water. The methods of open and closed recooling can be combined. The sampling site is located on the return side of the circulatory system.

Representative sampling locations throughout the system shall be defined for periodic microbiological/hygiene checks. Microbiological sampling guidance is given in ISO 19458. The sample is preferably taken from the circulating water between the running pump at the spraying/trickling stage. A sampling facility (sampling tap allowing disinfection, preferably by flaming, and draining) is to be provided at this location. Allow the water to drain for at least 30 s before sampling. Sampling shall be performed in such a manner that results are not distorted by biocide dosage. The sampling location shall be upstream of the point of biocide dosage.

If sampling is not possible at this location, the sample can be taken from the sprayed water or by bail sampling from the circulating-water basin[3].

Special cooling processes are usually used when the medium to be cooled is very hot (e.g. waste heaters, heat pumps) or when very low flow temperatures are required (e.g. brine cooling). For special cooling processes in the high temperature range (temperature > 100 °C), ISO 5667-7 shall apply.

6 Main types of waste water sampling

6.1 Spot sampling

In the case of spot sampling (refer Annex B), it is possible to implement:

a) direct sampling in the waste water body:

   1) directly by using laboratory bottles;

   2) using a ballasted sample collector equipped with laboratory bottles;

   3) using an automatic sampler.

b) indirect sampling in the waste water body:

   1) using a sampling rod equipped with a collection container;

   2) using a bucket or other equipment.

NOTE Spot samples are usually taken manually, but may be taken by automatic sampling equipment or by event-triggered automatic samplers.

6.2 Composite sampling

Composite sampling consists of several discrete samples. It can be done automatically or manually (refer Annex B).

For automatic composite sampling, there are several types of composite sample (see ISO 5667-1). It is possible to implement:

— constant volume variable time sampling (C.V.V.T)

— constant time variable volume sampling (C.T.V.V)

— constant time constant volume sampling (C.T.C.V)

For manual composite sampling, this approach is equivalent to sampling with fixed time, fixed flow and fixed volume.

7 Waste water sampling

7.1 General aspects

The client should clearly define the purpose of the sampling so that the sampling operative implements the appropriate sampling strategies.

7.1.1 Preparation of the sampling campaign

Controlled sampling is conditioned by good preparation of the sampling campaign and knowledge of the activity of the establishment, type and mode of operation.

Sampling operative should take all necessary steps to ensure that the coordinates and the feasibility of the operations requested are established beforehand. The use of a GPS and the exploitation of the photos and/or plans made available or the observations collected during the preliminary investigation make it possible to avoid any localization errors.

The sampling operative shall have at their disposal in their vehicles the procedures relating to sampling operations and measurements, as well as the notices specific to in-situ measurement apparatus (pH meter, conductivity, etc.).

All equipment (in-situ measurement apparatus, sampling equipment, refrigerated device) should have been checked. Use dedicated equipment for waste water sampling.

Laboratory bottles should be selected and prepared according to the type of analysis requested and respecting the packaging and preservation conditions prescribed by the laboratory.

Recordings of sampling operations (field form, label, other) should be prepared and possibly pre-filled.

Ensure the safety conditions (see Clause 12) before any intervention.

7.1.2 Arrival on site

It is important to confirm on site, the location of the points where the sampling operation will be carried out. In case of pollution identification, consider the extent of pollution.

If possible, the sample should be taken out below the surface of the water in order not to collect floating materials or fluids which cannot be representatively sampled. Avoid manipulations (such as transfer, shaking) of the samples to a minimum, as this may cause changes. The sample volume depends on the study programme and extent of analysis and can vary within wide limits from a few millilitres to many litres.

As a rule, floating substances and sedimented substances cannot be taken representatively out of flowing water. For identification, expediently they are taken in a separate sample; a poor quantification is often not useful.

When sampling out of sewers using ladles, care should be taken that the scoop is moved in the direction of flow under the surface of the water at a rate adapted to the flow. The opening of the scoop is in the flow direction.

To avoid contamination of the sample, make sure that the scoop does not touch the wall of the sampling manhole or the bottom of the sewer.

In many cases, pipes specially designed for sampling with a small nominal width, which either have a continuous flow of waste water or cooling water (by-pass line) or with a shut-off device (sampling device) are used. It is best to take the samples from vertical pipes in turbulent flow. When laying the sampling lines, longer horizontal pipe sections should be avoided. The length of the sampling lines should be at least five times the pipe diameter from the manifold to ensure a sampling in the fully mixed zone.

7.2 Composite sampling for waste water quality monitoring

7.2.1 General

The objective is to constitute a representative sample of the mass of water studied over a period of time, ranging from a few hours to a day or a week.

For selecting the sampling period over which a composite sample has to be taken, two factors should be considered:

a) The objective of the sampling. For example, it may be necessary to assess the average organic load in a flow over several 24 h periods, in which case flow proportional composite samples will be adequate.

b) The stability of the sample. In the example given in a), it would not necessarily be practical to extend the compositing period for longer than 24 h, since the organic component in the sample under study may deteriorate.

The overall sampling period may vary from a few hours, where tracing studies on volatile organics are being monitored, to several days, where stable inorganic species are being monitored.

The stability of the sample may often limit the duration of the sampling period. In such cases, reference should be made to the specific analytical techniques to be employed and the receiving laboratory should be consulted, in order that correct preservative measures can be used.

ISO 5667-3 gives further details on the preservation and storage of samples.

The sampling time depends, among other things, on the process stability of the waste water treatment plant, the nature of the statement to be made (instantaneous or average), and the durability of the parameters to be examined.

To detect concentration peaks in waste water with rapidly changing composition, carry out short-term sampling with high frequency. Take average samples to detect average loads over defined periods of time. In this case, continuous flow sampling is best suited. For discontinuous sampling, select the shortest possible intervals between the individual samples. They should not exceed 5 min for the 2-h mixed sample and 30 min for the 24-h mixed sample.

The duration of the sampling depends on the parameters specified in the water discharge permits. This information on the sampling duration (random sample, qualified random sample, 2-h mixed sample, 24 h composite sample) are based on legislation (e.g. waste water origin related annexes to the Waste Water Ordinance).

Composite sampling is generally carried out by means of automatic samplers or manually.

Sampling is usually carried out in a single container (constitution of an average sample) or in several containers (study variation of pollutant concentration over time).

7.2.2 Automatic composite sampling

Automatic sampling equipment can usually be programmed to carry out sampling either at constant volume (time proportional sampling) or at variable volume (flow proportional sampling).

7.2.2.1 General recommendations on use of an automatic sampler

For the installation and use of an automatic sampler, it is recommended to follow these points:

- **sampler positioning**: placing the sampler horizontally in a safe manner (see 12.3) and at an appropriate height above the sampling point (particularly for vacuum pump automatic sampler) and as close as possible to the body of water. Follow manufacturer's installation recommendations. The automatic sampler should collect the samples over the required height regardless of the positioning retained;

- **intake water pipe positioning**: select measurement sections where the flow is well mixed, homogeneous and always supplied with water.

- **sampling system and outlet tube to the container:**

— should be as short as possible, inert with regard desired substances and always in ascending position to prevent deposit formation (avoid bends, siphons, bearings);

— should have an internal diameter greater than or equal to 9 mm;

— should be arranged so that no part of sampled fluid is retained within the sample line;

— should be checked after each sampling event to ensure that no clogging of the pipe has occurred (e.g. purging the suction pipe).

- **strainer**: if a strainer still has to be used, it:

— should not be clogged by macro-waste (debris, larger solids, etc.);

— should have a mesh corresponding to the diameter of the suction pipe in order to prevent the sampling of large diameter solid materials;

— should be checked after each sampling event to ensure that no clogging of the strainer has occurred.

- **suction speed**: should not be less than 0,5 m/s to avoid segregation of the suspended matter in the sampling loop and thus avoid the risk of clogging.

NOTE 1 Lower suction speeds may be possible if proven satisfactory. An example where this is known to be the case is where the internal diameter of the suction pipe is 12 mm or more in which instance a suction speed of 0,3 m/s has been demonstrated to be acceptable[5].

NOTE 2 Users meet the national requirements where applicable.

- **unit volume:**

— should be appropriate to ensure representative sampling (e.g. at least 50 ml for vacuum pump or 25 ml for in-line plunger);

— bias shall not be greater than 10 %;

— repeatability shall not be greater than 5 %.

The resulting expended uncertainty U (k=2) shall not be greater than 15 % (see Annex I). Most automatic samplers are given a maximum of 5 % repeatability variation coefficient for a volume of 250 ml. If working with a lower volume, it should therefore be validated before implementation and checked if it fulfils the requirements.

NOTE The number of samples per hour required to get a representative sample is to consider. Users can refer to national guidance where applicable.

7.2.2.2 Automatic composite sampling, flow proportional sampling (C.V.V.T and C.T.V.V)

A flow proportional composite sample can be collected using one of two methods. One method consists of collecting a constant sample volume at varying time intervals proportional to the wastewater flow (C.V.V.T). For the other method, the sample is collected by varying the volume of each individual aliquot proportional to the flow, while maintaining a constant time interval between the aliquots (C.T.V.V).

These sampling methods are the most representatives of the body mass to be taken and are essential to characterize a flow of pollutants. It requires that the automatic sampler be connected to a flow meter.

There are two main types of flow measurement devices for controlling the sampling at the flow rate:

— devices in closed line with electromagnetic or ultrasonic sensors;

— devices in open-channel equipped with various sensors (ultrasonic, piezoresistive, bubble, height/speed).

Knowledge of the volume and variability of the effluent is required to programme the automatic sampler to take appropriate sub samples.

Depending on the capacity of the automatic sampler and the volume required for carrying out the analysis, the unit volume should be determined in conformance with the requirements (see quality assurance Clause 10).

7.2.2.3 Automatic composite sampling, time proportional sampling and reconstituted average sample in relation to flow

When the automatic sampler cannot be connected to the flow meter (due to incompatibility of the equipment or too great a distance between the two devices), when the flow and/or composition of the effluent is variable or for legal requirements, a time weighted sampling can be carried out. It is therefore necessary to build the composite sample (subject to the use of a multiple bottle automatic sampler).

For build the composite sample, it is necessary to collect in parallel the information related to the flow and/or the pollutant load (pH, conductivity, temperature, etc.).

Depending on the capacity of the automatic sampler, the volume required for the analyses, the constant time intervals and the unit volume should be determined in compliance with requirements (see 7.2.2.1).

The methodology to obtain a reconstituted average sample in relation of flow is as follows. The sampling operative homogenizes each individual bottle and takes, in to each individual bottle, a proportional volume at the volume flow. Take the largest volume in the individual bottle which is the most filled. For the other individual bottles, take the volume (ml) to be taken (V_n) in the bottle. n is a percentage relative of total volume (Formula 3):

$$V_n = \left[V_{\text{final}} \times \left(\frac{M^3{}_n}{M^3{}_{\text{total}}} \right) \right] \tag{3}$$

V_n: sample volume (ml) to take in the bottle n

V_{final}: total volume (ml) of the laboratory bottles

$M^3{}_{\text{total}}$: total volume discharged (M^3)

$M^3{}_{\text{n}}$: volume discharged during the sampling of the bottle n (M^3)

7.2.2.4 Automatic composite sampling, time proportional sampling (CTCV)

This method can be implemented, e.g. when the instantaneous flow of the effluent varies little over time (repeatability variation coefficient of 20 % on the average and if the information collected shows that the pollution load is not very variable during the period of sampling).

In this case, as flow rate is not relevant to time weighted composites, it is recommended that the samples are collected in a single bottle to avoid the transference stage.

7.2.2.5 Validation of the representativeness of composite sampling

The validation of the representativeness of the sampling is achieved by respecting the quality control criteria (see Annex H) before and after sampling campaign.

In case of deviation, the sampling organization will implement corrective actions, these actions will have to include informing the customer and the means put in place to remedy it.

Any information provided by the automatic sampler should be recorded (e.g. number of pulses transmitted by flow meter and number and volume of incremental samples taken, etc.).

7.2.3 Manual composite sampling

This method involves manually taking multiple discrete incremental samples without using an automatic sampler. The sampled volume of each discrete sample should be identical in order to obtain a representative sample.

The sampling equipment should be checked, and the repeatability variation coefficient of the sampling equipment should be lower than or equal to 5 %.

Then, all the discrete samples are mixed together in a larger container, homogenized and subsampled in laboratory bottles.

For sampling carried out regularly in tanks, it is possible to install a sampling system (sampling rod equipped with a valve, several sampling rods positioned at different heights, etc.).

7.2.4 Manual sample reconstitution

Each discrete sample, whether proportional or not proportional of the flow (see 7.2.2.3) is decanted into a larger inert container equipped if possible with a tap and a lid to avoid the outside contamination. Once all the samples are decanted into the same container, the whole composite sample is homogenized according to the recommendations defined in 9.1.

An example of the methodology of the manual sample reconstitution is shown in Figure 1.

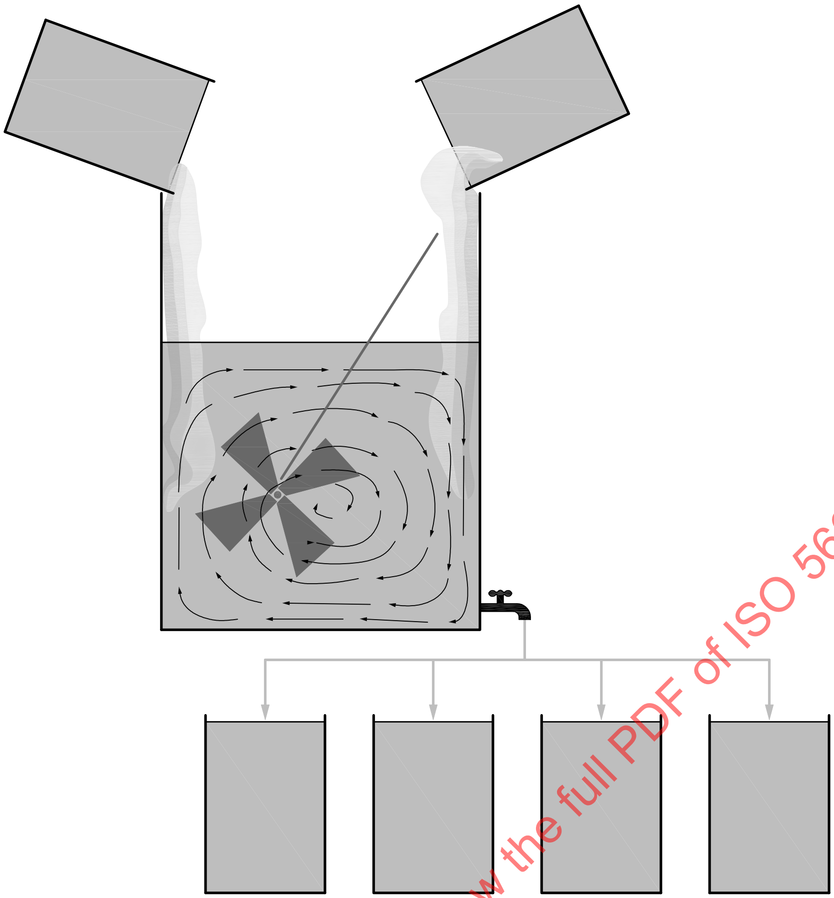


Figure 1 — Example of a manual sample reconstitution

This method should not be implemented when the sample is an automatic composite sample, volume or flow weighted, with a single bottle sampler. In this case, the homogenization is carried out directly in the single bottle sampler according to the recommendations defined in 9.1.

If the automatic composite sampling is carried out with a multiple bottle sampler, the above methodology (Figure 1) will be applicable.

Mixing should take place with the minimum entrainment of air.

7.3 Spot sampling in an effluent stream

7.3.1 General

Urban or industrial activities which discharge water to the sewers, show a great variability over time. Consequently, the nature of the dissolved or solid substances present and the pollutant load can vary considerably over time in waste water and this may be cyclical and/or random. For this reason, manual spot sampling of waste water is not the most appropriate sampling type, nor the most frequently used for representative sampling of raw sewage.

However, there are some circumstances where this type of sampling is useful, such as ongoing pollution events or emergency response in the event of accidental pollution (refer to Annex B). In the case of a waste water discharge (inlet, outlet of sewage treatment plant, sewer, industrial discharge), sampling should be carried out in the main channel, preferably away from the edges and obstacles present. The sampling equipment shall be placed in the main channel of the discharge. The opening or inlet of the sampling container will be oriented in the flow direction of the discharge.

Unless specified otherwise by the client or for a technical reason, the sampling is normally carried out at about 30 cm below the surface or at mid-height of the water column in a homogeneous zone to avoid taking the surface film or sediments.

It is important to check the absence of interfering elements (floating bodies) before and during the sampling period.

Do not rinse laboratory bottles with the body of water before sampling (refer to ISO 5667-3).

After sampling and once the laboratory bottles are closed (before they are stored and transported), if the outer wall is wet, rinse the walls of the laboratory bottles with clean water (e.g. drinking water, distilled water, etc.) or clean and dry with wipes.

If intermediate equipment is used, it should be cleaned in order not to contaminate the body water and the samples (refer to Annex C).

NOTE All the operations carried out and any anomaly observed are recorded on the field sheet (see Annex D).

7.3.2 Direct sampling

7.3.2.1 General

Direct sampling can be carried out either directly into laboratory bottles or with a bottle holder.

It is important to minimize oxygenation when filling laboratory bottles (e.g. using wide-opening bottles). For bottles containing a stabilizer, perform the sampling using another similar bottle as an intermediate and transfer the sampled water into the bottles containing the stabilizer, minimizing the oxygenation.

The sampling operative plunges the laboratory bottles directly into the body of water. The bottles without stabilizer are preferably immersed, the mouth downward, and then slowly rotated so that they are parallel to the flow, bottle mouth oriented in the direction of flow.

In most cases, fill the bottle to the top to exclude air, as gas exchange might rapidly change the quality of the sample. In some cases, such as when a solvent is added directly to the bottles, as in oil analysis for instance, the bottle should only be filled to the shoulder. Guidance on the filling level of the bottle should be sought from the laboratory.

7.3.2.2 Directly into the laboratory bottles

The laboratory bottles are opened and closed directly under the water to ensure they are completely full.

The sampling operative can use either a sampling rod equipped with the laboratory bottle or a ballasted sample collector equipped with laboratory bottles.

- **In the case of a sampling rod:** The sampling operative located at the edge of a structure (primary clarifier, outlet channel, etc.) adapts the length of the sampling rod so that the bottle reaches the main discharge channel.
- **In the case of a ballasted sampler:** The sampling operative positions themselves above the area to be sampled (e.g. sewer, sewer manhole). The length of the rope or chain of the ballasted sampler should be adjusted so that it dives to at half the depth height of the water column.

7.3.3 Indirect sampling

The indirect sampling consists of a sampling from sampling equipment or intermediate container into bottles.

7.3.3.1 From a sewer

Several materials are suitable for sampling from a sewer: bucket, pumps and flap bottles.

In all cases, the sampling equipment (system, rope) should be protected from all sources of contamination (e.g. do not place the rope on the ground).

7.3.3.2 From the edge of an open-air structure

The sampling operative, located at the edge of the open structure, adapts the length of the sampling rod so that the rod bottle (other than the laboratory bottle) reaches the main stream of flow (refer to 7.3.2).

7.3.4 Automatic, remote start or event-triggered sampling

Event-triggered automatic sampling based on realtime online monitoring of waste water parameters increases the chance of obtaining a representative sample of the actual waste water quality at that specific point in time.

7.4 Spot sampling of tanks — planned discharges

This involves taking a representative sample from the liquid effluent contained in a tank, to analyse it off-line in a laboratory. This operation is performed prior to the discharge authorization and is used to quantify the concentration of chemicals and/or the activity concentration of the various radionuclides.

NOTE This sampling method is currently used for nuclear effluents. The nuclear effluent is a very small part of waste water discharges but an important one. This technique can be applicable for industrial effluent too.

Prior to collecting the sample, the contents of the tank should be mixed for a period to be defined by the sampling operative (see 8.4).

So as not to modify and to retain the representative character of the sample, the following instructions shall be followed:

— keep mixing during sampling, and;

— take measures to prevent any effluent flowing into the tank between the start and the end of the sampling, until the end of the authorized discharge.

NOTE Certain recirculating pumps may require fluid inflow (public water or demineralised water) for sealing and/or cooling. This inflow can be recovered in the tank. In this case, this inflow is assessed in terms of its impact on the sample's representativeness.

Sampling involves several consecutive operations to be implemented to guarantee the best representativeness possible for the sampling:

— mixing of the contents to be sampled before and during sampling. The effectiveness of the mixing depends on the dimensions and shape of the tank, the physical-chemical composition of the effluent and the mixing method;

— rinsing the sampling rod or the recirculating line branch with the effluent to be collected. The rinsing duration shall correspond to at least the renewal of at least once the volume of the sampling system;

— filling the containers with the effluent at a high enough speed to limit deposits in the sampling system.

The representativeness of samples taken from a tank (new or existing) shall be justified. A description of the methods and tests used to estimate uncertainties relative to the sampling should be recorded.

To demonstrate the homogeneity of the effluents contained in the tank, certain relevant physical-chemical parameters (conductivity, suspended matter, salts, metals and organic compounds, for example) for the samples collected from various heights in the tank or for variable mixing durations are monitored to determine the minimum mixing duration to be observed to achieve a homogeneous effluent composition throughout the tank and guarantee sampling representativeness. The maximum tolerated deviation between two measurements of the parameter selected to satisfy the homogeneity criterion shall preferably be lower than 20 %.

The homogeneity of an effluent may also be assessed by monitoring changes to the concentration of a radioactive or chemical tagging agent added (sodium nitrate or chloride, lithium chloride, colouring agent, short-life radioactive element, etc.). The tagging agent used shall be suitable for the facility's operating restrictions and the environmental requirements.

For single-point sampling, the minimum stirring duration is determined by reaching a platform or stationary state defined by the measurement results from a series of samples distributed over time. In this case, it should be ensured that there are no dead zones when mixing.

When possible, checks should be performed on the representativeness of a sample, via continuously sampling from the discharge pipe, downstream of the tank, for the whole discharge duration. In this case, consistency (deviation lower than 20 %) between the parameter measurements chosen for the validation shall be observed. This measure shall be taken if there is no mixing before or during the discharge.

8 Sampling equipment

8.1 General

The nature of the materials of the sampling equipment will be chosen based on their compatibility with the target parameter and will have to guarantee the absence of physico-chemical interference with the parameters to be measured (see Annex E).

Do not use the following materials for samples of parameters at low concentration level[7]:

— material containing brass connections;

— pigmented plastic material (coloured plastic);

— non-food polyvinylchlorinated plastic material (PVC).

These materials are known to release metals (zinc, cadmium, etc.) and organic compounds. If these types of materials (PVC, metal) or other materials are used, then it will be necessary to demonstrate the absence of contamination or the adsorbance of the parameter(s) (see 10.3).

8.2 Automatic sampler

Automatic samplers can be fixed or portable and can also be equipped with a refrigerated chamber.

The automatic sampler shall have a closed compartment for filling and storing the collected samples in darkness, and a system enabling the samples to be kept at a temperature compatible with the preservation requirements in ISO 5667-3 for the whole duration of sampling, which may take several days. In some cases, and if required in agreement with the customer, the use of a non-refrigerated portable automatic sampler is possible (e.g. accessibility of the sampling point, analyte stability under ambient conditions).

Automatic samplers enable a certain amount of autonomy in terms of the sampling duration (up to several days) and therefore reduce the frequency of human sample collection operations. This capability shall not affect the quality of the collected samples.

Sampling of pumping systems can be carried out using different technologies [e.g. by vacuum pump (VAP), by means of a peristaltic pump (PP), by means in-line plunger or by using external pump systems]. The advantages and disadvantages of the two main types of samplers are presented in Annex F.

Whatever automatic sampler selected, the automatic sampler should comply with the safety conditions defined in 12.3. It should also be isolated, protected from extreme temperatures and precipitation.

The automatic samplers may use single containers to create a single average sample over a period, or multiple containers to create several samples over the given period.

The choice of automatic sampler should be adapted according to each sampling problem in order to either obtain the best representativeness of the sampling or to satisfy the specification provided by the customer (see 7.2.2.1).

The nature of the materials of the automatic sampler will be chosen based on its compatibility with the target component and will have to guarantee the absence of physico-chemical interference with the parameters to be measured (see Annex E).

When selecting automatic sampler, the user should also bear in mind that the operation manual should be easy to read, and in a language that is understood by and appropriate for the sampling operative. The availability of after-sales service and spare parts should also be considered. Finally, it is imperative that the equipment requirements for the supply of electricity or compressed air correspond to the availability of services at the location where the equipment is to be used.

8.3 Manual sampling equipment

8.3.1 General

The simplest equipment used for taking effluent samples consists of laboratory bottles, ballasted sample collector equipped with laboratory bottles, sampling rod equipped with a collection container or bucket. The volume should be appropriate to ensure representative sampling (minimum 25 ml).

When manual samples are to be used for the preparation of composite samples, the volume of the laboratory bottle, collection container or bucket should be well defined and known. The repeatability variation coefficient should be within ± 5 %.

Manual samples can also be taken with a vertical water sampler, consisting of a 1 l to 3 l volume tube with a hinged lid at each end of the tube, or other samplers operating on a similar principle [see Reference 4].

Manual sampling equipment should be made of an inert material that does not influence the analyses that will be carried out on the samples later (see ISO 5667-3).

Before starting sampling, the equipment should be cleaned (see Annex C) and checked (see 10.3). Detergents used should not contain substances that may influences the analyses to be studied.

The sampling equipment should be rinsed appropriately before the sampling and may be washed with demineralized/deionised water or tap water before use in the waste water stream from which the sample is taken to minimize the risk of contamination. Do not rinse the sampling equipment in the waste water when this will influence the analysis carried out later (e.g. analysis for oil and grease, raw and final effluents and microbiological analysis).

8.3.2 Ballasted sample collector

The equipment used could be a sampling rod or ballasted sampler. The sampling could be carried out directly with the equipment furnished with the laboratory bottles or indirectly with the equipment and a container. In this last case, it is necessary to transfer the contents of the container to laboratory bottles.

8.3.3 Bucket, vertical water sampler

When the sampling operation utilizes this type of equipment, the following precautions should be taken:

— do not use a rope for the submersible part and replace it with a cable or chain or by flexible wire covered in polytetrafluoroethylene (PTFE) or polyethylene that is easier to keep clean;

— reserve the equipment for this specific purpose. It should be carefully prepared before each sampling to avoid contamination of the samples taken (cleaning, etc.);

— keep the equipment cleaned whilst in storage and throughout the sampling.

8.4 Tank sampling equipment

8.4.1 Mixing

The mixing system is used to guarantee homogeneity regarding the contents of a tank prior to discharge and to collect a representative sample (see Annex A).

Ensure that mixing is effective and not result in stratification of the stirred effluent (for example, saline load producing sludge deposits that do not fully re-enter suspension via mixing or the presence of various non-miscible phases such as supernatants and emulsions). Mixing shall last for a predefined amount of time, to guarantee the homogeneity of the effluent in the container.

The mixing system in a container may be composed of one or more of the following systems:

— one or more mechanical agitators;

— bubbling via over-pressure (compressed air, for example);

— forced recirculation of the effluent (motive nozzle or pump, for example).

The materials used to construct the tank and the mixing and sampling system shall be inert with respect to the physical-chemical composition of the effluent.

8.4.2 Sampling equipment

The sampling system may be composed of the following main items:

— a sampling pipe equipped with a valve, used to collect the liquid at a certain distance from the inner wall of the tank. This device may be extended using a pipe, linking it to the sample container filling system. This pipe will be as short as possible to avoid the risk of deposits. Sampling may use gravity, a pump (peristaltic pump, for example) or any other suction system. The position of the end of the sampling pipe shall enable the most representative sampling possible to suit the chosen mixing method. Preferably, extreme positions shall be avoided (surface, edge and bottom of the container);

— several sampling pipe positioned at different heights. In this case, the final sample may be composed of a mixture of the samples in proportions to be determined, to form a composite sample;

— a ballasted sampler, equipped with a self-sealing opening/closing system in its lower part (ball, valve, etc.) to fill it to the desired level; and

— a by-pass or a branch on a recirculating line associated with a container.

NOTE It is advisable that the sampling operative utilises different sampling equipment such as rods or bailers for each effluent type (e.g. raw sewage, final effluents, industrial discharges, etc.).

Also see 8.3 (manual sampling equipment).

9 Homogenization, preservation, transport and storage of samples

9.1 Homogenization of collected volume

If the required sample volume is so large that several removals are needed and/or different bottles have to be filled with one sample, the homogeneity of the sample shall be ensured. This is especially important in samples containing particles and for the determination of analytes, which are enriched on solid particles.

Homogenization can be carried out on-site or at an on-site laboratory facility. If this step is performed incorrectly, it can cause differences in concentration of suspended solids in the bottles for the laboratory. Hydrophobic organic micro-pollutants have a great affinity with the suspended solids. Consequences of inadequate homogenization may be important (Figure 2).

For larger sample volumes (for example > 5 l), homogenizers with transportable sample vessels and with magnetic stirrer or mechanical stirrer should be used.

For lower volumes collected (≤5 l), the laboratory method can be applied (e.g. manual agitation, mixing using rods, etc.).

This step is essential, even for samples with a low suspended solid content. If manual homogenization is appropriate for the effluent being sampled because of exceptional circumstances, every effort should be made to ensure that the issues with settlement before subsampling do not occur.

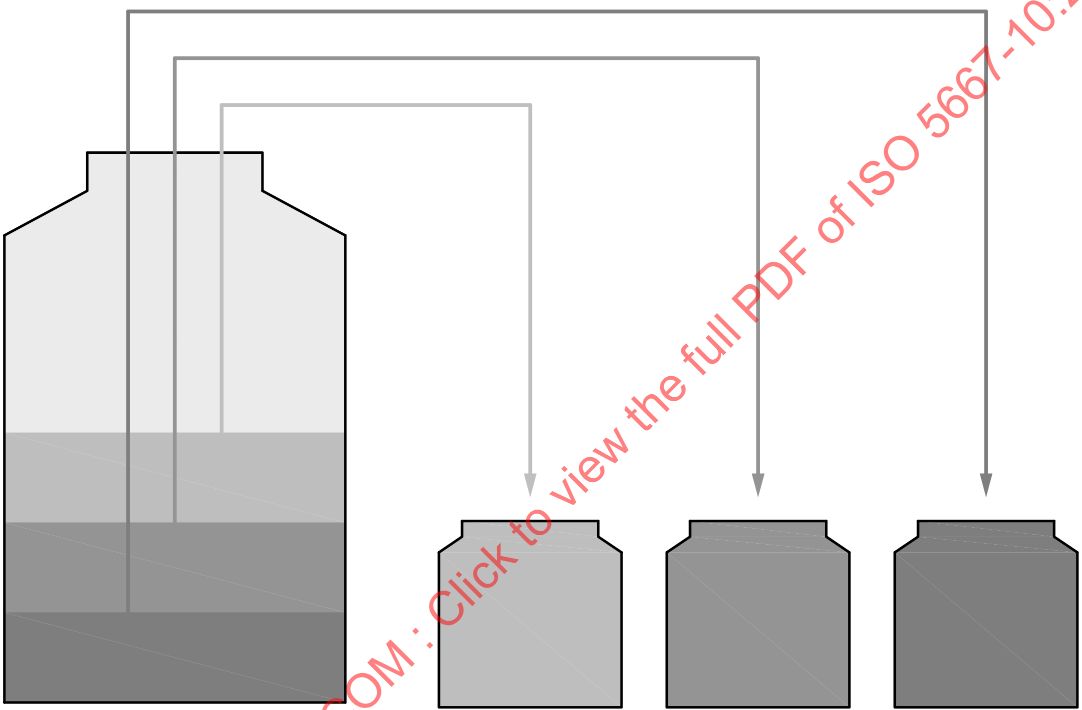


Figure 2 — Consequences of inadequate homogenization — different concentration suspended matter from one bottle to another

It is recommended to carry out the homogenization step, using a validated method. The effectiveness of homogenization method shall be checked (position of the propeller, speed of agitation, duration of homogenization). The maximum difference between two measurements for the parameter should preferably be <20 %. Refer to ISO 5667-14:2016, 7.4.4.

NOTE Ensure that sufficient volume of sample is taken to ensure it is representative for all the bottles to be filled.

9.2 Distribution of collected volume into laboratory bottles

For higher volumes collected (e.g. > 5 l) from the homogenized sample, the distribution to the different laboratory bottles should be carried out under continuous mixing. The distribution to the laboratory bottles may be done in a fractional manner or bottle by bottle. Annex G presents the advantages and disadvantages according to the type of distribution method chosen and its applicability according to the type of sampling and the sampling method implemented. In all cases where there is settlement likely, subsampling should take place immediately into the relevant laboratory bottles or containers.

NOTE Ensure that the representativeness of the sample is maintained during subsampling.

9.3 Preservation and packaging of samples

The type of laboratory bottles used for the collection and storage are given in ISO 5667-3 and should be defined in conjunction with the laboratory.

Some pre-treatments of the sample, via acidification, alkalising (for radioactive carbon, or metals for example), freezing or adding tagging agents may be required as soon as the sample is collected. Refer to ISO 5667-3.

The provisions set out by ISO 5667-3 should be observed to preserve and handle samples destined for the laboratory.

The collected sample is packaged in sealed containers, preferably made of plastic (polyethylene, etc.) or glass and, if necessary, designed to suit the counting geometry when the radiological analyses are conducted directly on the collected sample.

9.4 Transportation and reception

9.4.1 General

It is important to conform with the following general considerations regarding the transport of samples to the laboratory and comply with the requirements of ISO 5667-3, ISO 5667-16 and ISO 19458.

Procedures applied shall be in line with instructions from the laboratory and the requirements ISO 5667-3, ISO 5667-16 and ISO 19458.

The laboratory responsible for analysing the samples should always be consulted with regard to the selection of the preservation method and subsequent transport and storage.

9.4.2 Time

The maximum storage time of samples between the sampling and the analysis shall be in accordance with the requirements defined in ISO 5667-3, ISO 5667-16 and ISO 19458. Otherwise, any modification of this period should be justified.

In all cases, the maximum storage time of the sample should be agreed between the sampling agency, the laboratory and the customer.

9.4.3 Temperature

To ensure sample integrity between the sampling and the reception in the laboratory, samples should be stored in a cooling device capable of maintaining a temperature of (5 ± 3) °C. For proper evaluation of the conditions during transport, a device capable of recording the temperature of the air surrounding the sample may be used. At reception in the laboratory, samples should be stored according to ISO 5667-3, ISO 5667-16 or ISO 19458.

The quantity and size of the cooling device/s used should be adapted to the number of samples to be transported. The quantity and nature of the eutectic plates should be adapted to the temperature of the samples and the weather conditions.

NOTE The performance of the eutectic plates depends on the capacity of the fluid to restore the cold over time. To guarantee their effectiveness, they are packaged and used in accordance with the supplier's recommendations.

9.5 Security and traceability of samples during storage and delivery

9.5.1 Routine samples

The sampling operative has a responsibility towards the security and traceability of any samples, subsamples and sample registration documents in their care.

The sampling operative should check that samples, subsamples, labels, sample registration documents, etc., are undamaged and deposited in the designated place. If any containers are lost, damaged or broken in transit, this should be recorded by the sampling operative on the sample registration form.

If a courier is involved, then the courier should make a similar record while the samples are in his/her care. The courier should deliver the samples in accordance with laboratory instructions, especially if delivery takes place when the laboratory is unmanned.

9.5.2 Samples which might be used for legal purposes

Rules which should be followed if samples are to be used for legal purposes can be much more onerous, depending on the legal system operating in a particular jurisdiction.

Attention is drawn to the existence in some countries of national legislation, with which all persons involved at any stage in the sampling, storage or delivery of samples, or in the associated documentation, should be thoroughly familiar.

10 Quality assurance

10.1 Avoidance of contamination

Specific written instructions should be provided to the sampling staff on necessary protocols to follow to avoid contamination on sampling waste waters. Sampling staff should be encouraged to document any deviation to the foreseen risks to aid interpretation of results.

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

The nature of the materials of the sampling equipment should be chosen according to its compatibility with the analytes studied, and to guarantee the absence of physicochemical interference with the analytes to be measured. Annex E defines the nature of the materials for automatic samplers to be used with respect to the analytes to be measured.

Before departure from site, it is essential to prepare all the sampling equipment coming into contact with the sample and to ensure that the equipment is not released. A cleaning protocol is stipulated in Annex C.

All sampling equipment should be stored away from all sources of contamination (fuels, dust, road traffic, etc.). Similarly, sampling should be conducted in such a way as to avoid contamination of the sample. The use of suitable gloves (for example, powder-free nitrile gloves for single use) for all operations (sampling and sample conditioning) is required. It is strongly recommended during all sampling operations to limit the intermediate materials. However, if it is necessary to use intermediate equipment, it is imperative that this equipment is effectively rinsed prior to re-use and if the effluent being sampled requires it, it should be rinsed with water (e.g. drinking water, commercial water, ultrapure water) before any sampling.

All laboratory bottles used should be clearly labelled as soon as they are sampled, avoiding contamination of the sample (e.g. volatile compounds do not use markers containing solvents).

Procedures to monitor contamination and its control shall be followed in accordance with ISO 5667-14.

10.2 Sample identification and records

All the information should be reported in the field form, specifying environmental conditions, aspects of discharge, presence of any pollutants, any anomaly observed and precise coordinates or location of the sampling point(s). If the sampling is not possible, or if the location of the point should be modified to ensure the representativeness of the sampling, the client should be informed, and the information will be documented within field form (see Annex D).

All sampling equipment and procedures should be documented and recorded on an appropriate field sheet or in a logbook to facilitate accurate repeat surveys in accordance with the temporal scale on which the surveys are being undertaken. Sample containers should be clearly and unambiguously identified, so that subsequent analytical results can be properly interpreted. All details relevant to identification of the sample should be recorded on a label attached to the sample container.

Where the samples are identified through a pre-printed label with the site details and a unique machine-readable code, duplicated on both sample label and laboratory sample registration document, fewer details need to be recorded. Only details that can change, such as date, time and perhaps the operative's identification (which can be in the form of a signature), are required.

No further samples should be taken until all sample bottles have been labelled.

10.3 Assurance and quality control

Quality control measures the quality requirement of a process and uses techniques to correct any deviation from a process. Refer to ISO 5667-14 for full details of such techniques for use in waste water sampling.

All material coming into contact with the sample should be subject to quality control measures to ensure that there is no contamination and/or loss of analytes. These quality controls are to be expected when acquiring equipment or when modifying/adapting it.

Sampling equipment should be checked (Annex H). In the case of non-compliance, the deviations should be analysed. All these controls should be registered. These controls allow to master a possible drift of the equipment over time.

In the case of long or continuous sampling campaigns, the periodicity of quality controls may be adjusted in light of the above requirements.

11 Reports

11.1 Analytical reports

The detailed form of the sampling report depends on the objectives of sampling. All conditions that can influence the analytical results should be noted. Matters that could be considered for inclusion are:

— date and time of sampling (additionally mention date and time of the end of sampling for composite sampling, etc.);

— identity of the sampling operative;

— accurate identification of the sampling site and sampling location (address, description or photos, geographical coordinates, etc.);

— accurate description of the sampling point on the site (e.g. "outlet for the purification station channel 1", "sampling in the primary settling basin No. 1", etc.);

— number of elementary samples taken or not (in the case of composite sampling);

— type of sampling (composite, spot);

- results of in situ or on site physico-chemical measurements (e.g. water temperature, pH, etc.);
- implementation of quality controls (yes/no) and type of control if applicable;
- the information on any sample preservation technique used;
- the information on any sample filtration technique used;
- the information on any sample storage conditions;
- any deviations from standard protocols; and
- any observations and comments relevant to the interpretation of future analytical results (source of contamination observed during sampling, during preservation, reasons for location change, etc.).

In the case of an automatic sampler being used, it is also necessary to ensure the traceability of the following information:

- identification of the equipment used;
- programming used for sampling;
- parametric control of the conditions of use (suction speed, repeatability of the volumes taken, etc.);
- cleaned material (yes or no) before use;
- diameter of suction pipe in mm;
- length of suction pipe in m;
- suction speed;
- purges of the pipes (yes or no) before use;
- use of a strainer (yes or no);
- total volume collected;
- any observations and comments that may have been made on the automatic sampler that may interpret future analysis results.

An example of a sampling report protocol is given in the Annex D.

11.2 Sampling protocols

A “history” of changes to sampling protocols and procedures should be kept allowing a person examining the data the opportunity to evaluate the impacts of procedural changes in both the field and the laboratory on the series of observations collected. Laboratory changes such as detection limits and precision are usually recorded, but changes in sampling methods, sampling points and personnel should all be part of the record also. Sometimes this applies to a specific station, and at other times to an entire network. All too often the understanding of a data record is wrongly attributed.

12 Safety precautions

12.1 General

Points covered in this section are not exhaustive, they do not pretend to cover all situations. Safety is the responsibility of various people: client, sampling agency and subcontractor. However, taking security into account is an important aspect that can have a direct effect on the quality of the sampling operation.

The guidelines in this document cannot be substituted for local and/or national rules and regulations.

Risk associated with the sampling should be considered before any sampling takes place.

12.2 Personnel safety

The first concern of the sampling operative intervening on site (collective or industrial waste water treatment plant, industrial site, sewage network, etc.) should be of its safety and those of the persons present on or near the site. No technical operation, no facility, no cost, no delay, shall prevail over the safety of persons.

The sampling operative attending the site should ensure that the sampling area is secured as required by site protocols (e.g. by placing signs, etc.).

Dangers encountered at sampling sites can be very varied and each sampling operative should be trained and aware of all risks, such as: drowning, explosion, fall, poisoning, projection, burning (thermal, chemical, electrical), infection (microbiological risk), material used (battery, glass bottles, etc.), as well as to the preservatives and reagents present in the bottles provided by the laboratory (acids, bases, reagents).

During sampling, the sampling operative should wear personal protective equipment suitable for each of the risks to which he is exposed. These risks depend on the nature of the site, the sampling area, the sampling period and climatic conditions.

The personal protective equipment to be systematically used to carry out all sampling operations are: safety shoes and/or boots, helmets, goggles, disposable gloves and handling gloves, to guard against exposure risks to toxic or pathogenic materials (ingestion, inhalation, skin contact).

The personal protective equipment to be possessed according to dangers likely to be encountered are: emergency mask, gas mask, gas detector (H_2S, CO, O_2, etc.), safety harness, tripod, stop fall, alarm device for lone worker, chemical (solvents, hydrocarbons, etc.) resistant gloves.

The list of potential hazards and safety features can be established during the preliminary visit. The sampling operative should be trained and informed before carrying out the sampling operations. The identified risks can be formalized in a prevention plan.

In certain cases where there are specific risks, the sampling operation should be carried out by two persons to ensure safety and to raise the alert if there is a problem.

If the conditions of access or security to the sampling operative are not fulfilled, sampling should not be undertaken, and the client and the analytical laboratory should be informed.

12.3 Equipment safety

In the case of automatic samplers or sampling equipment installed on the site, adequate precautions should be taken so as not to expose them to natural hazards, theft or vandalism. Equipment installed on site should also not present a risk to the environment or to the public.

Sampling operations in confined spaces (basin, pipeline, tank, sewer) and in particular, sewage networks, require compliance with specific safety rules for the equipment.

Attention shall be paid to risks associated with the sudden rising of water in the sewers or in pipes that could damage or destroy the sampling equipment.

Foresee that when measuring the water height, the water height measuring device should not be under water when the flow is zero. In case of a sampling equipment, as the sampling line should stay under water to avoid pumping air, the measuring channel should include a side-sampling well which is always filled with water so that the sampling line will stay under water.

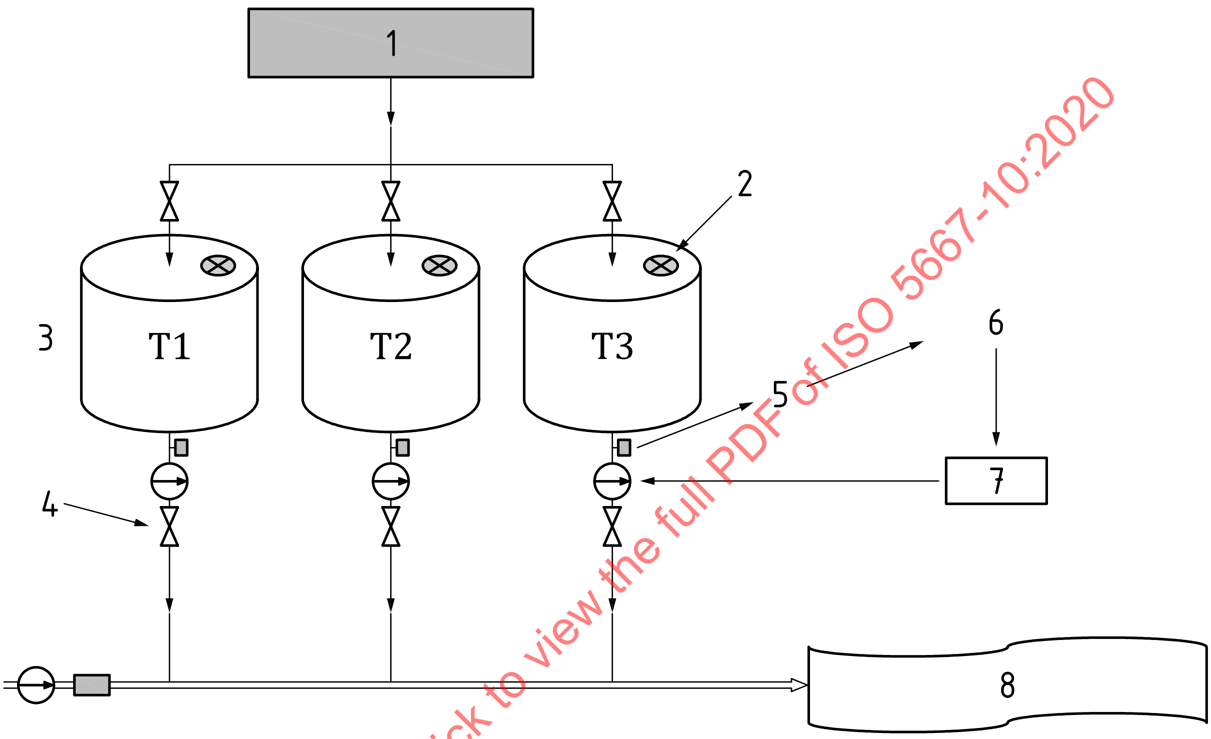
NOTE In cases where the height of the water level cannot be disturbed by flushing the sampling line of the automatic sampling equipment and if mixing is good just upstream of the obstacle, then the intake can be located there, taking care that sediment is not sampled and ensuring that the intake remains below liquid level.

The sampling equipment installation area should be clearly identified and tagged.

Under certain conditions, the customer may impose the use of specific materials [e.g. equipment for potentially explosive atmospheres (ATEX)]. The sampling equipment shall comply with the relevant requirement for the use of equipment in potentially explosive atmospheres in the case that sampling equipment are installed in a hazardous explosive atmosphere or where liquids are pumped from. Use safe equipment and refer to ISO standards on intrinsically safe equipment.

Annex A
(informative)

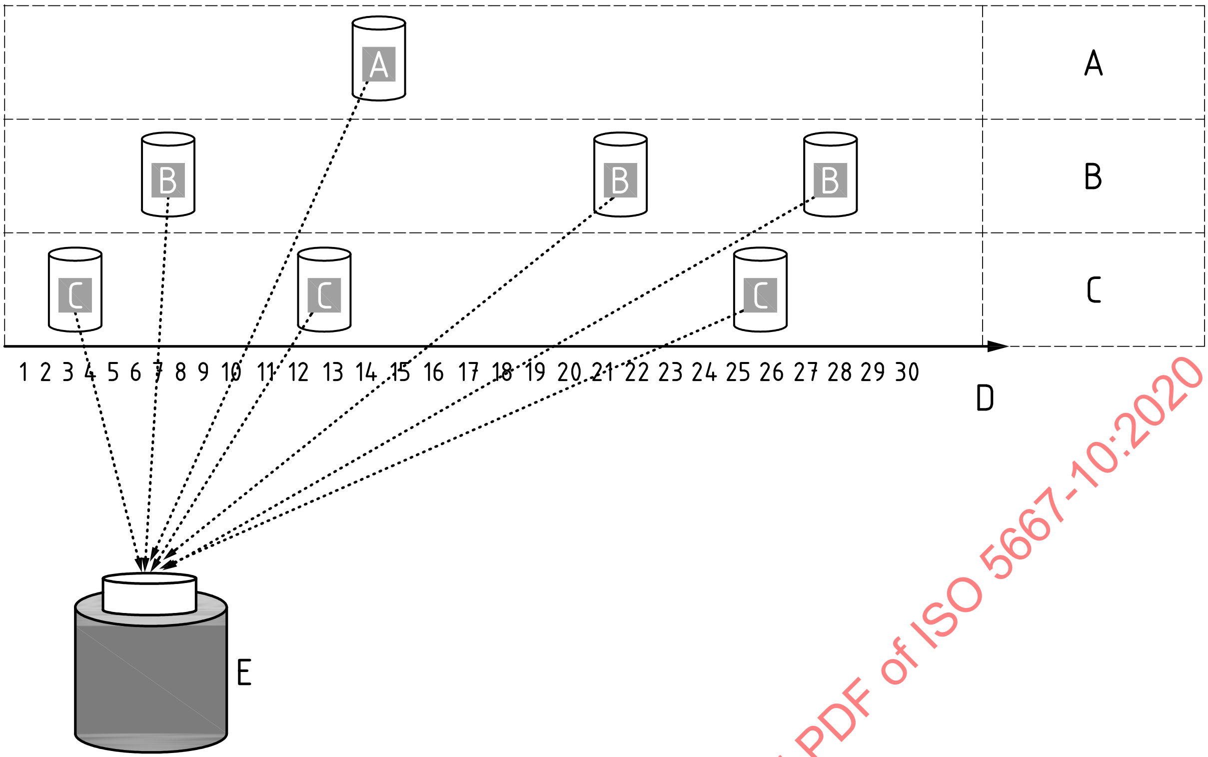
Examples of sampling from tanks



Key

1 production of liquid effluents (systems)
2 mixing system
3 temporary storage tanks prior to discharge
4 discharge pump
5 samples taken
6 off-line measurements in a testing laboratory
7 prior discharge authorization
8 discharge channel

Figure A.1 — Diagram showing sampling from tanks



Key

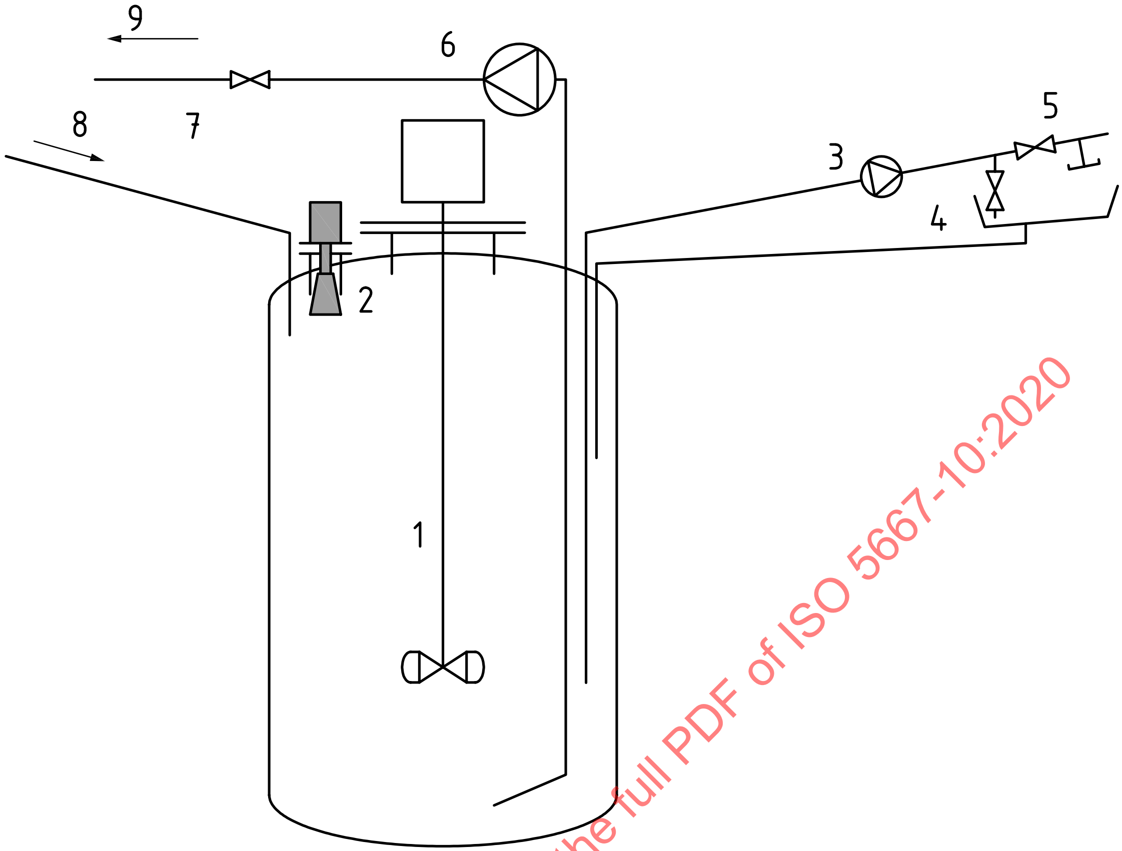
A tank number 1 B tank number 2 C tank number 3 D discharge date

E representative sample of monthly discharges (sample volumes proportional to the volumes of the tanks)

NOTE 1 Take account of the preservation durations suited to the analyses to be carried out.

NOTE 2 To create a composite sample, the sample volumes are determined based on the actual volumes discharged.

Figure A.2 — Example of creating a composite sample



Key

1 agitator
2 level sensor
3 sampling pump
4 chamber return tank and valve
5 sampling tank and valve
6 draining pump
7 chamber draining valve
8 effluent intake
9 to effluent output

NOTE 1 The chamber draining system is not shown.

NOTE 2 The other equipment (fan, inspection trap, high-level alarm, possible visual level, overflow, rinsing, associated retention, safety and handling systems, etc.) are not in the system.

Figure A.3 — Effluent chamber diagram

Annex B
(informative)

Advantages and disadvantages of main types of waste water sampling

The tables below present the advantages and disadvantages of these sampling methods and the context in which these different sampling methods can be implemented.

Table B.1 — Advantages and disadvantages of spot sampling of waste water

Type of sampling	Sampling method	Advantages	Disadvantages	Context
Spot Composition of effluent at an instant of time	Direct	Requires no intermediate material (directly in laboratory bottles) Quick and easy method	Not representative of a flow or load Not possible to use bottles with preservative agent	Accidental pollution Tanks Monitoring of waste water quality Monitoring of volatile compounds
	Indirect (If direct sampling is not possible)	Elimination of risks associated with interventions in the flow of waste water body	Risk of contamination of the sample due to the use of an intermediate Risk of contamination of intermediates during storage Longer method to implement Not representative of a flow	Accidental Pollution Tanks Possibility for monitoring the quality of the discharge water (special case: composite sample) Monitoring of waste water quality

Table B.2 — Advantages and disadvantages of automatic sampling of waste water

Type of sampling	Sampling method	Advantages	Disadvantages	Context
Composite	Manual	Time saving for a short-term sampling (1 h or 3 h) Little equipment implemented Simple method Qualified spot sample	Not representative of a flow in the absence of flow knowledge Risk of contamination of elementary samples before constitution of the final sample	Tanks Special installations [degreaser, de-oiler, cooling installations by dispersion of water in an air stream (cooling towers)] Monitoring of waste water quality
	Automatic Volume/ flow proportional sampling or other physical-chemical parameter (e.g. conductivity) (C.V.V.T / C.T.V.T)	Fastest technique to evaluate a pollutant flow Technique to be used for variable flow in chemical composition and/or flow	Required prerequisites: Know the hydraulic variability of the flow Select the volume interval between each sampling Choose the volume of each sampling Do not collect sufficient volume or overflow of the collected volume	Monitoring of waste water quality Possibility of accidental pollution Tanks
	Automatic Time proportional sampling and reconstituted average sample with respect to the flow rate	Technique to be used in case the automatic sampler cannot be connected to the flow meter Control of the volume collected	Prerequisites: Knowing and measuring hydraulic flow variability during sampling Longer method to implement due to the reconstitution of the weighted average sample at the flow rate Risk of sample contamination during the flow-weighted sample reconstitution step	Monitoring of waste water quality Tanks
	Automatic Time proportional sampling (C.T.C.V)	Technique easy to implement Technique to be used where the flow rate or composition of the effluent is not very variable over time Control of the volume collected	Technique not representative of a flow if the flow of the effluent varies in chemical composition and/or flow rate	Monitoring of waste water quality Tanks
Event triggered sampling	Automatic spot or composite sampling Direct or Indirect	Sampling based on real-time online monitoring of waste water parameters Representative sample of the event at the time Quick and easy method	Flow	Monitoring of waste water quality Pollution events

Annex C
(informative)

Example of cleaning protocol — Sampling equipment

C.1 General

Cleaning protocol should be applied before each sampling operation; it applies to all elements coming into contact with the water to be sampled (automatic sampler, pumping pipes, homogenization device). Cleaning should always be carried out between two sampling operations at two separate sampling points. It ensures that the sample that is taken is not contaminated.

In any case, the applied cleaning protocol implemented will have been validated by quality control. ISO 5667-14 describes the methodologies for the blanks implementation.

C.2 Conditions of realisation

Cleaning should preferably be carried out in a dust-free premise or laboratory. Attention should be paid to reagents used under routine conditions in laboratory (e.g. high mercury contamination for analysis of chemical oxygen demand) and use solvent-free markers. Use a clean work surface and protect the cleaned material.

If this operation is carried out outside, it is recommended to be not near sources of exhaust gas, aerosols, dust (e.g. parking vehicles, area of reagents delivery, handling mud). Do not smoke nearby.

When cleaning, pay attention to non-removable electrical elements, such as stepper motors, attached to certain distributor arms/trays (automatic multi-flask samplers). Use a mono-flask automatic sampler (without dispenser tray).

The following table includes (but is not limited to) items requiring regular maintenance and/or change:

Table C.1 — Items requiring regular maintenance and/or change

Automatic sampler	Cleaning: items to clean	Scheduled maintenance: items to replace
Vacuum Pump (VAP)	☐ Dispenser tray ☐ Sampling bowl ☐ Suction pipe ☐ Collecting flask	☐ Suction pipe ☐ Sampling bowl (If a crack forms)
Peristaltic Pump (PP)	☐ Collecting flask ☐ Suction pipe ☐ Crushing pipe to roller pump	☐ Suction pipe ☐ Crushing pipe to roller pump

C.3 Methodology

Regarding the parameters to be analysed, the cleaning protocol may be different (see Table C.2).

Table C.2 — Cleaning steps in function of type of parameters being sampled

<table>
<tr><th colspan="2">LOCATION OF THE CLEANING STEPS</th><th colspan="3">TYPE OF PARAMETERS TO BE SEARCHED</th></tr>
<tr><th>Without means of protection (as absence laboratory hood, etc.)</th><th>With means of protection (laboratory equipped hood, calcination oven, etc.)</th><th>Parameters _ Macro-pollutants</th><th>Metals</th><th>Micropollutants (organic and metallic substances)</th></tr>
<tr><td>Coarse cleaning with hot tap water</td><td>Coarse cleaning with hot tap water</td><td rowspan="3">Step 1</td><td rowspan="4">Step 2</td><td rowspan="6">Step 3</td></tr>
<tr><td>Washing with a solution of hot tap water and alkaline detergent (e.g. labwash®, detergent phosphate free)</td><td>Washing with a solution of hot tap water and alkaline detergent (e.g. labwash®, detergent phosphate free)</td></tr>
<tr><td>Rinsing with tap water</td><td>Rinsing with tap water</td></tr>
<tr><td>Washing with acidified water (e.g. acetic acid 80 %, diluted to ¼)

Rinsing with demineralised water (3 times)</td><td>Washing with acidified water, the acid nature for metals decontamination will be the responsibility of the laboratory (acetic acid, nitric acid or other).

Rinsing with demineralised water (3 times)</td><td rowspan="3"></td></tr>
<tr><td>Rinsing glass and polytetrafluoroethylene (PTFE) items with solvent for residue analysis (ultrapure acetone or hexane, for example)</td><td rowspan="2">Rinsing glass and polytetrafluoroethylene (PTFE) items with solvent for residue analysis (ultrapure acetone or hexane, for example) and rinsing with demineralised water (3 times)

OR

Calcination at 500 °C for several hours of glass items</td><td rowspan="2"></td></tr>
<tr><td>Rinsing with demineralised water (3 times)</td></tr>
</table>

NOTE 1 If cleaning and decontamination is carried out by an analytical laboratory, the acid nature for metals decontamination will be the responsibility of the laboratory (acetic acid, nitric acid or other). Similarly, during the organic substances decontamination stage, the laboratory can perform calcination at 500 °C for several hours for the glass items instead of ultrapure acetone or hexane rinsing.

NOTE 2 This cleaning protocol can also be used for the cleaning of equipment used in spot sampling operations (e.g. bucket, ballasted sample collector).

Annex D
(informative)

Example of field form — Waste water sampling

		SAMPLING IDENTIFICATION		
Sampling operative identity:			**Signature:**	
Date and time of beginning:			**Date and time of end:**	
Location of sampling:				
....				
Exact sampling point Identification:				
....				
Identification of client:				
Sampling purpose:				
waste water quality monitoring O			pollution identification O	
		SAMPLING CONDITIONS		
Sampling type	Spot O		Direct O	Indirect O
	Composite O		Manual O	
	Automatic O			
Sampling location	Sewer O		Manhole O	
	Channel O		Reservoir O	
	Collector O		Other O	
Equipment used	Laboratory bottle O		Ballasted sample collector O	
	Sampling rod with a container O		Bucket O	
	Automatic sampler O		Pump O	
Material used	Glass O	PTFE O	Polyethylene O	Stainless O
		MEASUREMENTS		
Physico chemical measurements		Continuous O		Spot O
	In-situ O	on site (spot sample) O		on site (Sub-sample of the volume collected) O
Temperature:		Water° C:		Air ° C:
pH (unity pH):	at °C	Conductivity 25 °C (µS/cm):		Redox potential (mV):
Turbidity:				
Other measurements:				
....				
		OTHER COMMENTS		

Field Form — Waste water sampling (after)

SPOT SAMPLING WITH PUMP			
SAMPLING PROCEDURE			
Pump type:	Date:	Start:	End:
Intake water positioning:		Intake water depth:	
Pumping flow (l/h):			
Duration of pump rinsing:		Duration of pumping for sampling:	
Other comments:			
....			
....			

MANUAL COMPOSITE SAMPLING			
Equipment type:			
Equipment cleaning before using	Yes O	No O	
Intake water positioning:		Intake water depth:	
Date:	Start:	End:	
Unit volume (ml):	Volume repeatability ≤ 5 %:		No O
Interval of subsamples:	Total composite sample volume:		Yes O
Other Comments:			
....			

AUTOMATIC COMPOSITE SAMPLING		
Automatic sampler type:	Reference:	
	Mono-flask O	Multi-flask O
Pumping type:	Peristaltic O	Vacuum O
Automatic sampler cleaning before using	Yes O	No O
Pipe purging before using	Yes O	No O
Intake water positioning:	Intake water depth:	
Speed suction (m/s):	Programming type:	
Flowmeter reference:	Date of last quality control:	
Running (date and hour):	Start:	End:
Suction pipe:	Diameter (mm):	Length (m):
Unit volume (ml):	Total composite sample volume:	
Volume repeatability ≤ 5 %:	Yes O	No O
Volume bias to ≤ 10 %:	Yes O	No O
Presence of a strainer:	Yes O	No O
Refrigerated automatic sampler:	Yes O	No O
Automatic sampler temperature:	Start value:	End value:
Other comments:...		