
Water quality — Sampling —

Part 23:

**Guidance on passive sampling in surface
waters**

Qualité de l'eau — Échantillonnage —

*Partie 23: Lignes directrices pour l'échantillonnage passif dans les eaux
de surface*

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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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 5667-23 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee 6, *Sampling (general methods)*.

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

- *Part 1: Guidance on the design of sampling programmes and sampling techniques*
- *Part 3: 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*
- *Part 14: Guidance on quality assurance of environmental water sampling and handling*
- *Part 15: Guidance on the preservation and handling of sludge and sediment samples*
- *Part 16: Guidance on biotesting of samples*

- *Part 17: Guidance on sampling of bulk suspended solids*
- *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*
- *Part 21: Guidance on sampling of drinking water distributed by tankers or means other than distribution pipes*
- *Part 22: Guidance on the design and installation of groundwater monitoring points*
- *Part 23: Guidance on passive sampling in surface waters*

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Introduction

Passive sampling devices can be used for monitoring concentrations of a wide range of analytes, including metals, inorganic anions, polar organic compounds (e.g. polar pesticides and pharmaceutical compounds), non-polar organic compounds (e.g. non-polar pesticides), and industrial chemicals (e.g. polyaromatic hydrocarbons and polychlorinated biphenyls) in aquatic environments.

Pollutant levels in surface water have traditionally been monitored by spot sampling (also known as bottle or grab sampling). Such sampling gives a snapshot of pollutant levels at a particular time. Pollutant levels in surface water have a tendency to fluctuate over time and so it may be more desirable to monitor pollutants over an extended period in order to obtain a more representative measure of the chemical quality of a water body. This can be achieved by repeated spot sampling, continuous monitoring, biomonitoring or passive sampling.

Passive sampling involves the deployment of a passive sampling device that uses a diffusion gradient to collect pollutants over a period of days to weeks. This process is followed by extraction and analysis of the pollutants in a laboratory.

Passive sampling devices can be used in kinetic or equilibrium modes. In equilibrium mode, the passive sampling device reaches equilibrium with the sampled medium, and provides a measure of the concentration at the time of retrieval from the environment. In the kinetic mode, the passive sampling device samples in an integrative way, and provides a measure of the time-weighted average concentration of a pollutant in the water over the exposure period. Where uptake into the receiving phase is under membrane control, then passive sampling devices operate as integrative samplers between the time of deployment and an exposure period of up to the time to half maximum accumulation in the receiving phase. Membrane control means that the transport resistance of the membrane is larger than that of the water boundary layer. In stagnant water, uptake is generally controlled by the water boundary layer. Under highly turbulent conditions, uptake is membrane controlled. Where uptake is controlled by the water boundary layer, then the passive samplers behave in a manner similar to those where uptake is under membrane control, but the sampling rate depends on flow conditions. Where flow conditions vary over time, uptake can be under water boundary control when turbulence is low, but change to membrane control when turbulence increases.

Diffusion into the receiving phase is driven by the free dissolved concentration of pollutant, and not that bound to particulate matter and to large molecular mass organic compounds (e.g. humic and fulvic acids). This technique provides a measure of the time-weighted average concentration of the free dissolved fraction of pollutant to which the passive sampling device has been exposed. For some passive sampling devices for metals, the concentration of analyte measured includes both the free dissolved fraction and that fraction of the analyte bound to small molecular mass inorganic and organic compounds that can diffuse into and dissociate in the permeation layer. Pollutant bound to large molecular mass compounds diffuses only very slowly into the diffusion layer. The concentration measured by a passive sampling device can be different from that measured in a spot (bottle) sample. In a spot sample, the fraction of pollutant measured is determined by a combination of factors such as the proportion of pollutant bound to particulate matter and to large organic compounds, and the treatment (e.g. filtration at 0,45 µm or ultrafiltration) applied prior to analysis. Passive sampling devices used in surface water typically consist of a receiving phase (typically a solvent, polymer or sorbent) that has a high affinity for pollutants of interest and so collects them. This receiving phase can be retained behind, or surrounded by, a membrane through which the target analytes can permeate. A schematic representation of such a passive sampling device is shown in Figure 1. In its simplest form, a passive sampling device is comprised solely of a naked membrane, fibre or bulk sorbent which acts as a receiving phase. In such passive sampling devices, the polymer acts as both receiving phase and permeation membrane. The polymers used in these passive sampling devices usually have a high permeation, and uptake is controlled by the water boundary layer. Uptake comes under membrane control only at very high flow rates. Different combinations of permeation layer and receiving phase are used for the different classes of pollutant (non-polar organic, polar organic, and inorganic). Passive sampling devices are designed for use with one of these main classes of pollutant.

Passive sampling devices can be used in a number of modes including qualitative or semi-quantitative which can be applied in the detection of sources of pollution, for example. When appropriate calibration data are available, passive sampling devices can also be used quantitatively for measuring the concentration of the free dissolved species of a pollutant.

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Water quality — Sampling —

Part 23:

Guidance on passive sampling in surface waters

1 Scope

This part of ISO 5667 specifies procedures for the determination of time-weighted average concentrations and equilibrium concentrations of the free dissolved fraction of organic and organometallic compounds and inorganic substances, including metals, in surface water by passive sampling, followed by analysis.

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 5667-23:2011](https://standards.iteh.ai/catalog/standards/sist/857b2d65-1161-4b3a-af8b-7db48200f1da/iso-5667-23-2011)

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

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

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-9, *Water quality — Sampling — Part 9: Guidance on sampling from marine waters*

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

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

ISO/TS 13530, *Water quality — Guidance on analytical quality control for chemical and physicochemical water analysis*

ISO 14644-1, *Cleanrooms and associated controlled environments — Part 1: Classification of air cleanliness by particle concentration*

3 Terms and definitions

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

3.1 analytical recovery standard
compound added to passive sampling device receiving phase prior to analysis and whose recovery levels during analysis are used to provide information about recovery efficiency

3.2 field control
quality control passive sampling device to record any chemical accumulated in passive sampling devices during manufacture, assembly, storage, transportation, deployment, retrieval and subsequent analysis

3.3 passive sampling
sampling technique based on the diffusion of an analyte from the sampled medium to a receiving phase in the passive sampling device as a result of a difference between chemical potentials of the analyte in the two media: the net flow of analyte from one medium to the other continues until equilibrium is established in the system, or until the sampling period is terminated

3.4 integrative phase of passive sampling
phase of sampling during which the rate of uptake of an analyte into the receiving phase of the passive sampling device is approximately linear, and during which the uptake of the passive sampling device is proportional to the time-weighted average concentration of an analyte in the environment

3.5 performance reference compound PRC
compound that is added to the sampler prior to exposure and has such an affinity to the sampler that it dissipates from the sampler during exposure, and that does not interfere with the sampling and analytical processes

NOTE 1 The offloading (elimination) rates of PRCs are used to provide information about *in situ* uptake kinetics of pollutants.

NOTE 2 Currently PRCs are available neither for passive sampling devices for metals nor for polar organic compounds.

3.6 reagent blank
aliquot of reagent used in treatment of passive sampling devices which is analysed following deployment in order to diagnose any contamination from the reagents used

3.7 recovery spike
quality control passive sampling device, pre-spiked with known mass of analytical recovery standard, used to determine the recovery level of pollutant from passive sampling devices following deployment

3.8 passive sampling device class
class of passive sampling device based on the class of pollutant which a passive sampling device is designed to accumulate

NOTE Passive sampling device classes include:

- polar organic compounds;
- non-polar organic compounds;
- inorganic compounds, including metals.

3.9**membrane control**

where diffusion through the membrane of the passive sampler dominates the overall mass transfer and resistance to mass transfer of analytes from the bulk water phase into the receiving phase

3.10**water boundary layer**

viscous sub-layer of water adjacent to a surface, caused by complex hydrodynamic interactions of a surface with water, that causes resistance to diffusion from the bulk phase of water to the receiving phase, and that reduces in thickness with increasing turbulence in the bulk phase of water

3.11**sampling rate**
 R_s

apparent volume of water cleared of analyte per time, calculated as the product of the overall mass transfer coefficient and the area of the receiving phase exposed to the external environment

NOTE Sampling rate is expressed in litres per day.

3.12**deployment device**

structure to which passive sampling devices can be attached, or in which they can be contained during deployment, and that is suitable for ensuring that the passive sampling devices are retained in position at the deployment site throughout the deployment period

EXAMPLES A metal mesh, a pole or a cage, with mooring lines, buoys and anchors where necessary.

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4 Principle

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The general features of a passive sampling device are illustrated in Figure 1. The structures of the types of passive sampling device for the different classes of pollutants, polar organic, non-polar organic, and inorganic (including metals), are summarized in Table A.1. The procedures commonly used to calibrate the various designs of passive sampling device are summarized in Table A.2.

Pollutants accumulate in the receiving phase of a passive sampling device over a measured period of time of exposure to surface water. The pollutants are extracted from the passive sampling device in the laboratory and the amount of each pollutant accumulated is determined by chemical analysis.

Uptake of a pollutant into the receiving phase of a sampling device follows a first order approach to a maximum (see Figure 2). The mass accumulated after an exposure time, t , m_t , is given by Equation (1):

$$m_t = m_{\max} [1 - \exp(-k_e t)] \quad (1)$$

where

m_{\max} is the maximum mass accumulated;

k_e is a first order macro rate constant (the overall exchange rate constant) that depends on the properties of the sampler and the pollutant (see Note).

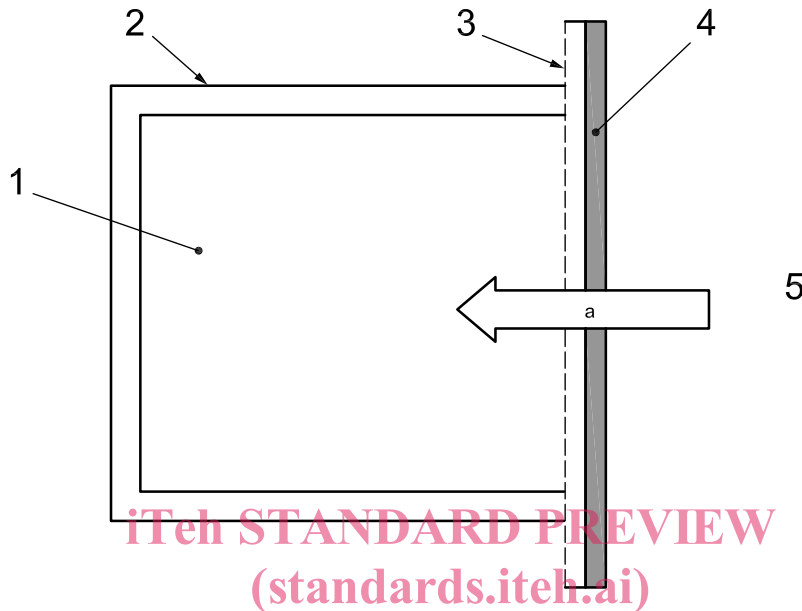
NOTE The parameters that make up the macro rate constant, k_e , are discussed in Clause 13.

Uptake is approximately linear with time throughout the exposure period between time of deployment, $t = 0$, and the time to half maximum accumulation in the receiving phase, $t = t_{0.5}$. Under these conditions, and providing that the mass transfer of pollutant is linearly related to the concentration in the water, then the passive sampling device operates in integrative mode and can be used to measure the time-weighted average concentration of pollutant to which the passive sampling device was exposed.

The time to half maximum accumulation in the receiving phase, $t_{0,5}$, is calculated using Equation (2):

$$t_{0,5} = \frac{\ln 2}{k_e} \tag{2}$$

At longer exposure times, as m_{max} is approached, the passive sampling device operates in equilibrium mode, and provides a measure of the concentration only at the time of retrieval of the passive sampling device.



Key

- 1 receiving phase
- 2 housing
- 3 permeation membrane
- 4 water boundary layer
- 5 water
- a Diffusion of pollutant.

NOTE 1 The permeation membrane and water boundary layer constitute the permeation layer.

NOTE 2 In some passive sampling device designs, the housing is replaced by a membrane that completely encloses the receiving phase. In some passive sampling devices (e.g. polyethylene strips or silicone rubber sheet) the receiving phase is not held in a housing but is deployed naked on a holding frame. In these passive sampling devices, there is no permeation membrane, but the water boundary layer acts as a permeation layer. For more information on individual types of passive sampling devices, see References [1] to [8].

Figure 1 — Schematic representation of a passive sampling device

5 Handling passive sampling devices

5.1 General

5.1.1 Ensure safety precautions are in place and adhered to for handling all chemicals.

5.1.2 It is essential that passive sampling devices be kept isolated from potential sources of contamination at all times except when being exposed at the sampling site. Ensure that the passive sampling devices are stored and transported in gas-tight containers, of inert materials relevant to the pollutants of interest.

5.1.3 Avoid physical contact with the receiving phase or membrane of the passive sampling devices, since this may affect the results. Where handling is unavoidable, use powder-free vinyl or latex gloves. Do not re-use gloves.

5.1.4 For some passive sampling devices, it may be necessary to avoid or at least minimize exposure to airborne contaminants during the handling, manipulation and deployment of passive sampling devices, and the subsequent analysis.