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Water quality — Sampling —

Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling

Qualité de l'eau — Échantillonnage —

Partie 14: Lignes directrices pour le contrôle de la qualité dans l'échantillonnage et la manutention des eaux environnementales

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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.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 6, *Sampling (general methods)*.

This second edition cancels and replaces the first edition (ISO 5667-14:1998), which has been technically revised.

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

— *Part 1: Guidance on the design of sampling programmes*

— *Part 3: Preservation and handling of water samples*

— *Part 4: Guidance on sampling from lakes*

— *Part 5: Guidance on sampling of drinking water*

— *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 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 water, waste water and related sludges*

— *Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling*

— *Part 15: Guidance on preservation and handling of sludge and sediment samples*

— *Part 16: Guidance on biotesting of samples*

— *Part 17: Guidance on sampling of suspended sediments*

— *Part 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 design and installation of groundwater sample points*

— *Part 23: Guidance on passive sampling in surface waters*

Introduction

Sampling is the first step in carrying out chemical, physical and biological examinations. Therefore, the goal of sampling should be to obtain a representative sample for the research question and to supply it to the laboratory in the correct manner. Errors caused by improper sampling, sample pre-treatment, transport and storage cannot be corrected.

This part of ISO 5667 specifies quality assurance and quality control procedures and provides additional guidance on sampling of the various types of water covered in the specific parts of ISO 5667.

Quality control procedures are necessary for the collection of environmental water samples for the following reasons:

a) to monitor the effectiveness of sampling methodology;

b) to demonstrate that the various stages of the sample collection process are adequately controlled and suited to the intended purpose, including adequate control over sources of error such as sample contamination, loss of determinand and sample instability. To achieve this, quality control procedures should provide a means of detecting sampling error, and hence a means of rejecting invalid or misleading data resulting from the sampling process;

c) to quantify and control the sources of error which arise in sampling. Quantification gives a guide to the significance that sampling plays in the overall accuracy of data; and

d) to provide information on suitably abbreviated quality assurance procedures that might be used for rapid sampling operations such as pollution incidents or groundwater investigations.

This part of ISO 5667 is one of a group of International Standards dealing with the sampling of waters. It should be read in conjunction with the other parts of ISO 5667 and in particular with parts 1 and 3.

The general terminology is in accordance with that published.

Water quality — Sampling —

Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling

WARNING — Consider and minimize any risks and obey safety rules. See ISO 5667-1 for certain safety precautions, including sampling from boats and from ice-covered waters.

1 Scope

This part of ISO 5667 provides guidance on the selection and use of various quality assurance and quality control techniques relating to the manual sampling of surface, potable, waste, marine and ground waters.

NOTE The general principles outlined in this part of ISO 5667 might, in some circumstances, be applicable to sludge and sediment sampling.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 5667-3:2012, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
accuracy
closeness of agreement between a test result or measurement result and the true value

Note 1 to entry: In practice, the accepted reference value is substituted for the true value.

Note 2 to entry: The term accuracy, when applied to a set of test or measurement results, involves a combination of random components and a common systematic error or bias component.

Note 3 to entry: Accuracy refers to a combination of trueness and precision.

[SOURCE: ISO 3534-2:2006, 3.3.1]

3.2
bias
difference between the expectation of the test results or measurement result and a true value

Note 1 to entry: Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the true value is reflected by a larger bias value.

Note 2 to entry: The bias of a measuring instrument is normally estimated by averaging the error of indication over an appropriate number of repeated measurements. The error of indication is the: "indication of a measuring instrument minus a true value of the corresponding input quantity".

Note 3 to entry: In practice, the accepted reference value is substituted for the true value.

[SOURCE: ISO 3534-2:2006, 3.3.2]

3.3
precision
closeness of agreement between independent test/measurement results obtained under stipulated conditions

Note 1 to entry: Precision depends only on the distribution of random errors and does not relate to the true value or the specified value.

Note 2 to entry: The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

Note 3 to entry: Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[SOURCE: ISO 3534-2:2006, 3.3.4]

3.4
representativeness
extent to which the condition of all the samples taken from the body of water reflects conditions in water of interest

3.5
blank
observed value obtained when measurement is made on a sample identical to the sample of interest, but in the absence of the determinand

Note 1 to entry: Deionised water; distilled water can be used as blank samples which are prepared in the laboratory prior to sampling.

3.6
field blank
container prepared in the laboratory, using reagent water or other blank matrix, and sent with the sampling personnel for exposure to the sampling environment to verify possible contamination during sampling

[SOURCE: ISO 11074:2005, 4.5.3]

3.7
spike
known quantity of determinand which is added to a sample, usually for the purpose of estimating the systematic error of an analytical system by means of a recovery exercise

3.8
recovery
extent to which a known, added quantity of determinand in a sample can be measured by an analytical system

Note 1 to entry: Recovery is calculated from the difference between results obtained from a *spiked* (3.7) and an unspiked aliquot of sample and is usually expressed as a percentage.

3.9
control chart
chart on which some statistical measure of a series of samples is plotted in a particular order to steer the process with respect to that measure and to control and reduce variation

Note 1 to entry: The particular order is usually based on time or sample number order.

Note 2 to entry: The control chart operates most effectively when the measure is a process variable which is correlated with an ultimate product or service characteristic.

[SOURCE: ISO 3534-2:2006, 2.3.1]

3.10
Shewhart control chart
control chart with Shewhart control limits intended primarily to distinguish between the variation in the plotted measure due to random causes and that due to special causes

Note 1 to entry: This could be a chart using attributes (for example, proportion nonconforming) for evaluating a process, or it could be a chart using variables (for example, average and range) for evaluating a process. Examples are:

a) X-bar chart — the sample means are plotted in order to control the mean value of a variable;

b) R chart — the sample ranges are plotted in order to control the variability of a variable;

c) s chart — the sample standard deviations are plotted in order to control the variability of a variable;

d) s^2 chart — the sample variances are plotted in order to control the variability of a variable;

e) C chart — the number of defectives (per batch, per day, per machine, etc.) is plotted.

[SOURCE: ISO 3534-2:2006, 2.3.2, modified — Note 1 to entry has been added.]

3.11
action limits
control limits between which the statistic under consideration lies with a very high probability when the process is under statistical control

Note 1 to entry: Action lines are drawn on a control chart to represent action limits.

Note 2 to entry: When the measure plotted lies beyond an action limit, appropriate corrective action is taken on the process.

Note 3 to entry: These limits are based on the assumption that only 0,3 % of normally distributed results will fall outside these limits. Such an occurrence would strongly indicate that additional, assignable causes of variation might be present and that action might be required to identify and reduce them.

[SOURCE: ISO 3534-2:2006, 2.4.4, modified — Note 3 to entry has been added.]

3.12
warning limits
control limits between which the statistic under consideration lies with a high probability when the process is under statistical control

Note 1 to entry: Warning lines are drawn on a control chart to represent warning limits.

Note 2 to entry: When the value of the statistic plotted lies outside a warning limit, but within the *action limit* (3.11), increased supervision of the process, to pre-specified rules, is generally required.

Note 3 to entry: The limits are calculated from the standard deviation of the statistic under consideration of at least 10 samples. Warning and action control limits are applied to individual sampling results.

[SOURCE: ISO 3534-2:2006, 2.4.3, modified — Note 3 to entry has been added.]

3.13
uncertainty
measurement uncertainty
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand based on the information used

[SOURCE: ISO/IEC Guide 99:2007, 2.26, modified — The notes to entry are not included here.]

3.14
true value
value which characterizes a quantity or quantitative characteristic perfectly defined in the conditions which exist when that quantity or quantitative characteristic is considered

Note 1 to entry: The true value of a quantity or quantitative characteristic is a theoretical concept and, in general, cannot be known exactly.

[SOURCE: ISO 3534-2:2006, 3.2.5, modified — Note 2 to entry is not included here.]

3.15
accepted reference value
value that serves as an agreed-upon reference for comparison

Note 1 to entry: The accepted reference value is derived as:

a) a theoretical or established value, based on scientific principles;

b) an assigned or certified value, based on experimental work of some national or international organization;

c) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or technical group;

d) the expectation, i.e. the mean of a specified set of measurements, when a), b) and c) are not available.

[SOURCE: ISO 3534-2:2006, 3.2.7]

4 Sources of sampling error

Sources of sampling errors include the following:

a) Contamination

Contamination can be caused by sampling equipment materials (sampling containers and sample containers) by cross-contamination between samples and by sample preservation and inappropriate storage and transport arrangements.

b) Sample instability

The type of sampling vessels and containers used can affect the stability of the determinand between sampling and analysis due to the inherent instability of the sample itself and the conditions in which samples are stored and transported.

c) Incorrect preservation

The choice of sampling vessels and containers affects the integrity of the determinand and the options for preservation which may be available, as detailed in ISO 5667-3.

d) Incorrect sampling

Deviation from the sampling procedure, or the procedure itself, might be a source of error.

e) Sampling from non-homogenized water bodies

f) Sample transportation

Figure 1 illustrates various sources of sampling error: environment, personnel, materials, methods, preservation and transportation. Further examples of common sources of sampling error are given in Annex A.

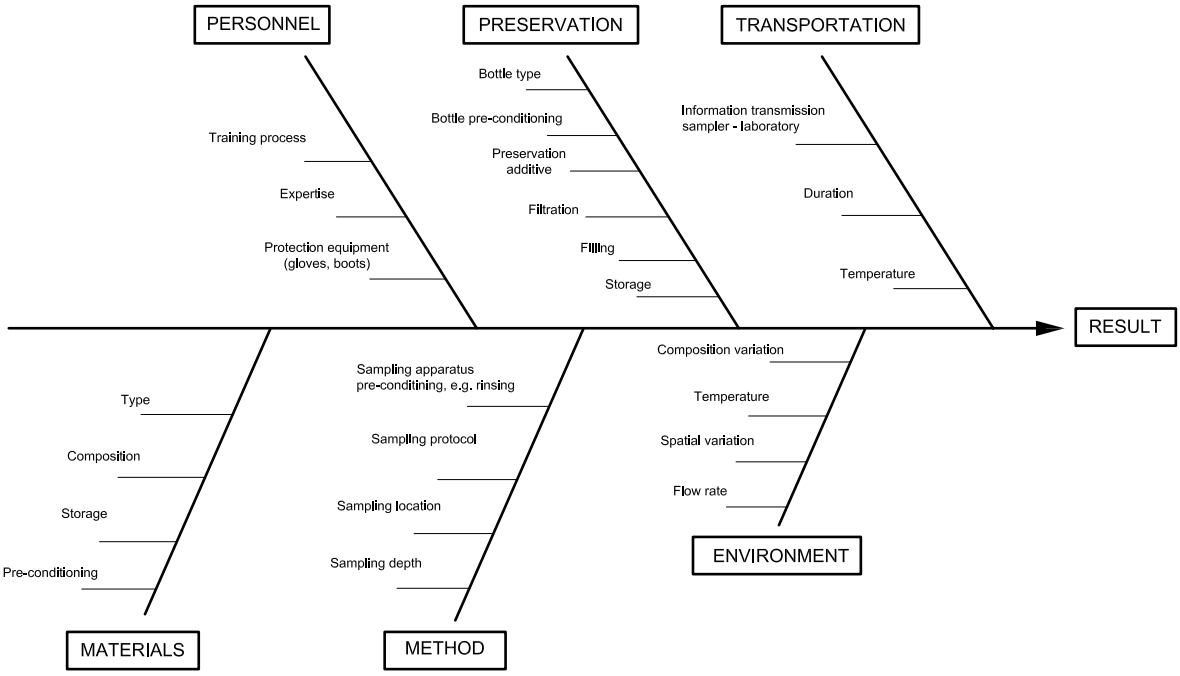

Figure 1 — Sources of sampling error

5 Sampling quality

5.1 General

A programme to establish sampling quality should be established for every series of sampling, so as to ensure that data resulting from sampling programmes are both trustworthy and scientifically credible. Mistakes in any step of the sampling procedure can result in substantial errors within the resulting data.

Laboratories that analyse collected samples usually have rigorous programmes of quality assurance and quality control (QA/QC) as required by national regulation and conforming to ISO/IEC 17025. However, such laboratory programmes of QA/QC cannot substitute for the rigorous sampling quality programmes required for the collection and handling of samples prior to delivery to laboratories for analysis.

Sampling quality programmes comprise all the steps taken to ensure that valid results are produced. Sampling quality programmes include documented evidence that the individuals who collect samples are competent and well trained, that appropriate sample collection and sample handling methods were employed, that equipment were maintained and calibrated, that correct practices were followed and that records are both complete and secure. It is important to establish a quality assurance programme and quality control effective for the characterization and reduction of errors. Depending on the objective (e.g. to check for any contamination of the sample at different points in the sampling procedure, and identify potential problems), the quality control set up will be different. See Table 1.

Table 1 — Means of quality control for different objectives

Objective	Means to implement
Check the absence of contamination	Blank environmental, Field blank, Transport blank, Equipment blank, Filter blank
Calculate the sampling precision	Duplicate sample
Check the stability of the sample	Spiking

Particular importance should be given to careful measurement of analyses performed on-site and to correct recording of determinand results. Reference should be made to ISO/TS 13530 regarding

analytical quality control for water analysis and to ISO 15839 regarding online sensors/analysing equipment for water.

Since analysing laboratories have expertise regarding QA/QC, it is suggested they be actively involved in the design and evaluation of sampling quality programmes.

5.2 Technical and personnel requirements

To take a sample correctly, adequate and cleaned equipment [such as sample containers, sampling devices, filtration equipment, a homogenizer, an intermediate container (funnel, spoon), and measurement equipment for on-site analysis] should be held in sufficient numbers. Regular maintenance of all equipment should be guaranteed.

The sampling vehicle and the facility should be equipped in accordance with the requirements for sampling (laboratory vehicle).

The sampling personnel should have relevant professional training, e.g. completed vocational education as a chemical laboratory assistant or specialist for waste water engineering. An essential prerequisite is appropriate initial job-training and regular training of sampling personnel. Participation in internal and/or external training should be documented (see 5.4).

A regular exchange of information between client, sampling personnel and laboratory personnel improves the quality of sampling and testing. All the necessary information for a sampling of ensured quality should be placed at the sampling personnel's disposal.[7]

5.3 Sampling manual

5.3.1 For sampling, the general requirements related to the competence of testing and calibration laboratories should be applied.

Procedures or operating instructions should be prepared and should include the following issues:[7]

a) sampling (matrix-based);

b) on-site measurement;

c) pre-treatment of samples;

d) preservation of samples (parameter-based);

e) sample transport, storage and sample delivery/reception.

Each person responsible for collecting water samples should carry an up-to-date sampling manual on-site. This manual should provide specific guidance regarding the sampling methods to be employed, sample handling and preservation, analytical methods for measurements to be performed at the sampling site, procedures to be followed when transporting samples to the laboratory and method details pertaining to any online continuous sensor type equipment to be utilized. It is suggested that the sampling manual should additionally detail all quality assurance procedures to be employed when collecting samples, when taking on-site measurements, when transporting samples to laboratory and when using or checking continuous monitoring equipment.

5.3.2 The sampling manual should specify:

a) the types of bottles or containers, their closures and the specific purposes for which they are to be used;

b) where relevant, the cleaning procedure and shelf life for bottles, containers and closures used for each parameter, including the amount and type of preservative to be added (e.g. first draw, flushed, stagnation) and the procedure for collecting samples for different parameters;

c) the sampling procedure for each parameter, including the type of sample to be collected;

d) the frequency and order of sampling;

e) the conditions of storage and transport of samples and the maximum time that can elapse before analysis should commence for each parameter; and

f) the description of preservation reagents (including usual colour), plus appropriate safety measures in case of spill, or contact with skin or eyes.

It is recommended that the manual additionally provide guidance as to appropriate sampling responses when unusual conditions are identified, plus a contingency plan for emergency conditions.

NOTE If laptop computers are used in the field, it is convenient to have electronic versions of manuals. Using electronic templates and spreadsheets can reduce errors in recording information and provide automatic calculations.

5.4 Training of sampling staff

All sampling staff should be fully trained before being allowed to work unsupervised. Training should include if relevant:

a) principles and practices of water supply and distribution;

b) principles and practices of water supply hygiene;

c) introductory knowledge in the field of interest, e.g. of water chemistry and of microbiology;

d) knowledge of water supply vulnerabilities to contamination including case studies of genuine contamination events with emphasis upon faecal contamination;

e) experience in all aspects of sampling;

f) supervised experience with laboratory techniques if staff are expected to take analytical measurements or to operate online monitoring equipment;

g) review of this part of ISO 5667 plus review of relevant clauses of reference standards; and

h) the full content of the sampling manual with special emphasis on identifying and safely coping with or avoiding potential hazards.

Once trained, all sampling staff performance should be subject to regular review. Monitoring and review procedures, criteria for satisfactory performance and policy on retraining should be documented. This training should be updated on a regular basis. More detailed information about requirements for training of personnel is given in ISO/IEC 17025.

A training record should be produced for each staff member detailing the training given, with dates and assessment of competence, results of evaluation reviews, retraining or further training given and any re-assessment of competence. An annual review of such training is considered the minimum.

6 Strategy and organization

6.1 Time, duration and frequency of sampling

The purpose of sampling is to obtain a representative sample for the study goal. This refers to:

a) the temporal representativeness;

b) the local representativeness; and

c) the applicable sampling technique.