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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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Contents

Page

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.

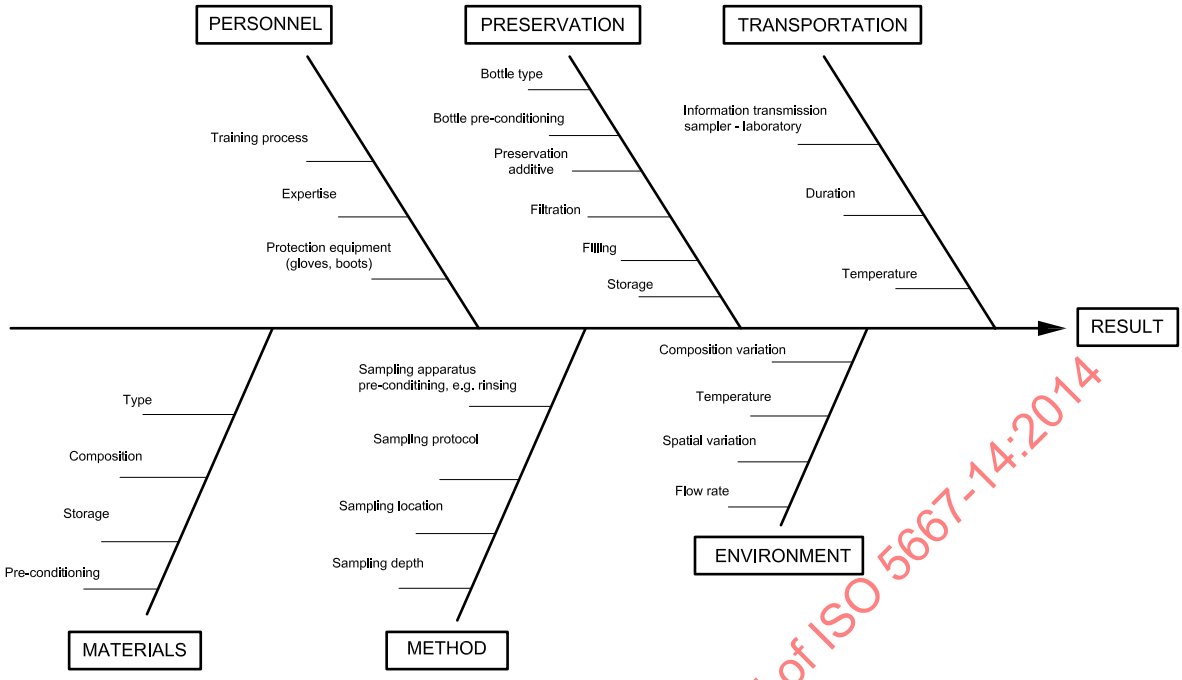


Figure 1 — Sources of sampling error

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.

This assumes that the sampling is carefully planned with respect to the expenditure of time, the appropriate vehicle and equipment as well as the professionally qualified staff needed.[7]

Time, duration and frequency can vary widely in the investigation of, for example, waste waters, surface waters and groundwaters. Their appointments are based on legislation, issues or other circumstances. For further information, see ISO 5667-1 and the type of water-specific standards of ISO 5667-series.

6.2 Sampling collection locations

To get a first idea of the sampling point, it is useful to review existing documentation. The documentation is defined by the position coordinates (easting and northing values). It includes maps (overview and detail), and photos (taken in different seasons if necessary). In practice, the GPS navigation handsets with topographical maps have proved useful.[7] For further information, see ISO 5667-1 and the type of water-specific standards of ISO 5667-series.

It is absolutely necessary to check the sampling point according to the local circumstances. Only on-site is it possible to assess whether a sampling point is representative for the area to be examined and the research in question, and whether the sampling point is easily accessible.

7 Sample collection and handling

7.1 Equipment and vehicle check prior to carrying out a sampling programme

The sampling personnel should receive a clearly formulated sampling order. Then the sampling is prepared on the basis of the operating instructions. To provide the materials and equipment as well as their preparation for sampling, the responsibilities between client, laboratory and sampling personnel should be clearly defined.[8]

The main steps of preparation for sampling are:[7]

a) provision of cleaned sampling equipment, intermediate container and devices for sample pre-treatment (homogenization, filtration);

b) provision of cleaned sample containers and their seals in sufficient numbers according to the examined parameters/parameter groups. It should be ensured that the containers are transported closed; no changes can be allowed to occur to the parameters/parameter groups that are to be examined due to the material of the containers by contamination, adsorption, diffusion or outgassing;

c) provision of material (e.g. labels for labelling the sample containers);

d) provision of material for sample preservation and the necessary dispensers;

e) provision of sampling documents consisting of sampling order, sampling protocol and sampling point documentation;

f) provision of and preparation of equipment for on-site measurements (e.g. temperature, oxygen, pH-value, conductivity, turbidity and test solutions required for on-site testing);

g) provision of appropriate protective and safety equipment;

h) provision of valid access authorizations (e.g. special permits, trafficability allowances, company ID cards, keys);

i) preparation of the sampling vehicle with regard to operating and traffic safety; cleanliness, and refrigeration unit of the vehicle

j) slip-resistant and damage-free loading of devices and equipment in the sampling vehicle-storage devices (as equipment *in situ*, boxes, …) with good distribution in the vehicle.

7.2 Preparation for sampling on-site

It is important to:

a) verify the accuracy of sampling location (coordinates, sampling point number, exact position [e.g. bank (left/right), river-centre];

b) monitor the sampling conditions (date, time, weather, specifics on and in the waters, if necessary record water level and flow);

c) select sampling equipment and sample containers by type and material;

d) ensure that cleaned equipment is used at each sampling. It is useful to have a number of sampling devices readily available. If this is not possible, the sampling devices should be cleaned by pre-rinsing with sample material or deionized water to prevent any carryover of sample constituents. In certain cases (e.g. high concentration of solid matters or visible presence of oils and fats), sampling devices may not be pre-rinsed with sample material;

e) check the marked sample containers for correctness and completeness or to label permanently.

7.3 Field measurements

The on-site measurements should be performed before the actual sampling, since they might still be able to give instructions that should be followed for sampling. The measurements can either be performed directly in the medium to be sampled, or in a spot sample to be discarded after the measurement. In scoop or sample collection containers, sensors or electrodes should not be used in combination because the use of various sensors could contribute to the contamination of the sample.[8]

It is important to ensure that on-site instruments are regularly calibrated. Functional tests and calibrations as well as the type of documentation are set for each parameter in the operation instruction. On-site verification of equipment *in situ* before and after series of measurement should be performed.

Measure and record the temperature of the sample on the site. Physical parameters (for example pH, dissolved gases, suspended solids) should be determined on-site, or as soon as possible afterwards. The pH-measurement in ion-poor waters with low buffering capacity or in saline waters requires special measuring conditions. For certain oxygen sensors, a minimum flow or agitation should be guaranteed. Provide alternative sensors in case of breakage.

The results of these operations (metrological control of field devices, management of calibration solutions) should be recorded and stored.

7.4 Taking the samples

7.4.1 Spot samples

Spot samples are needed to capture the current state with regard to time and/or location from a body of water. They should be taken in particular when a short-term change in the concentration of the analytes to be determined is to be expected in the sample. The reasons for this can be strong outgassing, faster degradation, adsorption or contamination. When scooping the sample by means of suitable devices, these effects are reduced.

The direct filling of the spot sample into the sample container should be favoured. The material of the vessel used should be selected according to the study parameters. Contamination of the sample by liquid or solid deposits to the sampling equipment should be excluded.

For further information, see ISO 5667-1 and the specific standards appropriate to the type of water under study in the ISO 5667-series.

In some cases, the sample container should be closed airtight and with no gas space above the liquid after filling.

7.4.2 Composite samples

To collect a composite sample, several spot samples are taken over a certain period of time. These are mixed by hand or by an automatic sampling device which collects samples continuously or discontinuously. When using automatic sampling systems, care should be taken that no substances settle in the pipeline systems. All the water-carrying parts of the pump, the hoses or pipes and associated sampling equipment should be manufactured from a material that does not change the sample with respect to the analytes to be determined.

Pressure side-acting pumps (submersible pumps) should be preferred to vacuum systems to minimize an outgassing of volatile substances. The pump should be self-lubricating to prevent the leakage of lubricant into the water or into the sample.

For automatic sampling with continuous and discontinuous working devices on-site, specific quality assurance procedures should be set by the operator, e.g. as outlined below:[7]

a) position of the water abstraction point;

b) type of pump (suction or pressure);

c) material of all water-carrying parts (pump, pipes/hoses including couplings, sampling device);

d) time intervals and sample volumes of increment samples;

e) cooling/freezing/preservation;

f) transferring the composite samples after homogenization into the sample containers; and

g) cleaning and maintenance of equipment.

7.4.3 Sampling pre-treatment

As water samples can be subject to very fast changes due to biological activity and chemical reaction processes in terms of their ingredients, immediately after sampling, appropriate preservation or pre-treatment measures should be performed. The type of sample pre-treatment and preservation should be set for each parameter or parameter group in a 'container and preservation plan" and included in the standard operating procedure. Sampling staff should adhere to conservation guidelines provided by the laboratory.

7.4.4 Homogenization and subsampling

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

For large sample volumes, homogenizers with transportable sample vessels and with magnetic stirrer or mechanical stirrer should be used for waste water sampling

Depending on the scope of investigation, the following variants arise.[7]

a) Subsampling from a bucket

   In practice, sampling with a bucket has proven easy to do. A precondition is that all subsamples can be filled out of it and there is no inhomogeneity in the spot sample. The sample is collected using a suitable vessel and then distributed to the various sample containers. The subsamples for the parameters in which a dependency from suspended matters exists (such as heavy metals, total phosphorus) are bottled in priority. If necessary, the scooped sample should be gently homogenized between the individual filling operations by means of an appropriate stirring rod.

b) Subsampling using a homogenizer

The single scoop samples are first placed in a sufficiently large collection vessel from which the various sample containers (subsamples) will be filled after gentle, continuous and complete mixing by a dispensing tap.

For collecting, mixing and filling large sample volumes, homogenizers with transportable sample vessels and with a magnetic stirrer or a mechanic stirrer are well suited as they are used for waste water sampling. During filling of sample containers, gentle stirring should be continued, gas exchange should thereby be avoided.

To demonstrate the homogeneity of the sample in the container, monitor the relevant physico-chemical parameters (e.g. suspended matter, metals, organic compounds) on samples taken at different heights in the container

— to determine the duration of homogenization to achieve a homogeneous composition of the effluent into the container, and

— to ensure the representativeness of the sample.

The maximum difference between two measurements for the parameter chosen to satisfy the homogeneity criterion should preferably be <20 %. For details, see the example in Annex C.

To avoid changes due to excessive air input, the sample containers for the determination of certain volatile parameters should be filled until they are overflowing, allowing at least two volumes to overflow and then immediately stoppered and checked to ensure the absence of air bubbles.

7.4.5 Filtration

In some cases, the goal of sampling is the determination of soluble components (e.g. metals, nutrients, DOC). Some requirements are given in ISO 5667-3:2012, 6.2 (*on-site filtration*). For this, it is advisable to separate the 'dissolved' component from the 'particulate' one already at the sampling site prior to transport to the laboratory. In this way changes in the composition that may otherwise occur after sampling prior to any treatment in the laboratory or the analysis can be minimized. If filtration is not possible on-site, the samples should be filtered immediately after receipt of the sample in the laboratory. If operations for solids separation (e.g. filtration, sedimentation, centrifugation) are required, this should be principally done before preservation.

The selection of the filtration methods depends on the examination spectrum. The corresponding instructions of the individual standards should be considered.

For on-site filtration, portable filtration devices using membrane filters (e.g. 0,45 µm) together with disposable syringes have been used. Rinsing the filter in the laboratory or on-site is necessary for certain parameters which might be contained in the filter due to its material.[8] The filter material should be examined regularly for blank values prior to its use for sampling.

For the monitoring of dissolved priority metals, it is recommended that the filtration of water samples take place under standardized conditions in the immediately after sampling on-site, because significant losses by adsorption to container walls are likely to occur in a very short time, especially in samples with high contents of suspended matter.[9]

7.4.6 Sampling preservation

The requirements for preservation in the individual analytical determinands is documented in ISO 5667-3. This forms the basis for the preparation of a "container and preservation plan". The specifications of ISO 5667-3 hold if they do not differ from specifications given in other standards.

For samples which are not treated with preservatives, the sample containers should be filled and closed immediately to minimize cross contamination from external sources (see paragraph below)

It is essential to ensure that any preservatives are accurately prepared and dispensed. The sample containers for chemically preserved samples (exclusively for the same examinations) should be used and marked accordingly. Avoid confusing labelling and contamination of the closures. Care should be taken with the durability of the preservative.

When preparing bottles containing preservatives, it is recommended that the preparation of containers be carried out in a sequence that minimizes the risk of introducing bias due to contamination of the determinand of interest by the substance used for preserving another determinand in the suite of analysis. For example, the use of chloroform as a biocidal agent in the preservation of samples for specific applications should not take place in the same environment as that where bottles are required for the collection of samples for chlorinated solvent screening.

Quality assurance samples used for transportation, stabilization and storage should be treated with the same processes as test samples. In addition, identification information on sample labels for quality assurance samples should ensure anonymity of identification as QA samples.

8 Sample identification

Each sample container should be clearly and durably marked. Do not use markers with solvent (risk contamination of the sample). The label may include, for example, the following information:

a) sample number;

b) sampling point;

c) date and time;

d) preservative, where applicable information about type and amount of addition; and

e) pre-treatment of the sample on-site (e.g. filtered).

For certain parameters (groups), it makes sense to use clearly recognizable sets of sample containers to avoid cross-contamination.

9 Field sample protocol

Describe each sampling point. In the case of a long-term programme, conditions which are agreed and remain unchanged need not be restated. In this case, only a statement of the *in situ* measurements and variables such as weather conditions and unusual observations need be recorded, e.g.:

a) deviations from the sampling order;

b) abnormalities and particularities of the sampling;

c) exceptional anthropogenic uses (discharges, water withdrawals); and

d) deviations from the operating procedures.

When abnormalities occur, it is useful to supplement the protocol with sketches and photographs.

When sampling for special reasons, detailed information should be given, including the reasons for sampling and any preservation steps taken.

10 Transport and storage of samples

The sample transport and receipt in the laboratory is the connection between sampling and analysis.

The requirements in the individual analytical standards in conjunction with ISO 5667-3 form the basis for the transport and storage of sample. The specifications of ISO 5667-3 hold if they do not differ from specifications given in other standards.

The samples should be delivered, if possible, to the laboratory on the same day as sampling. During transport, transport conditions prescribed in the analysis procedure (e.g. refrigerated) should be observed. Sampling and analysis should remain within the time set for the respective analysis methods. The filled sample containers should be transported to the laboratory in such a way as to be frost and shatter proof, and protected from heat and light and in accordance with the 'container and preservation plan'. This is to ensure and confirm the sampling protocol.

The samples and sampling protocols should be passed by the sampling personnel properly to a responsible employee of the laboratory or respective specimen collection point. If this is not possible, the samples should be stored in an appropriate manner.

11 Sampling quality control techniques

11.1 General

Sampling is defined in ISO 5667-1 as the process of removing a portion, intended to be representative, of a body of water (or sludge or sediment) for the purpose of examination for various defined characteristics.

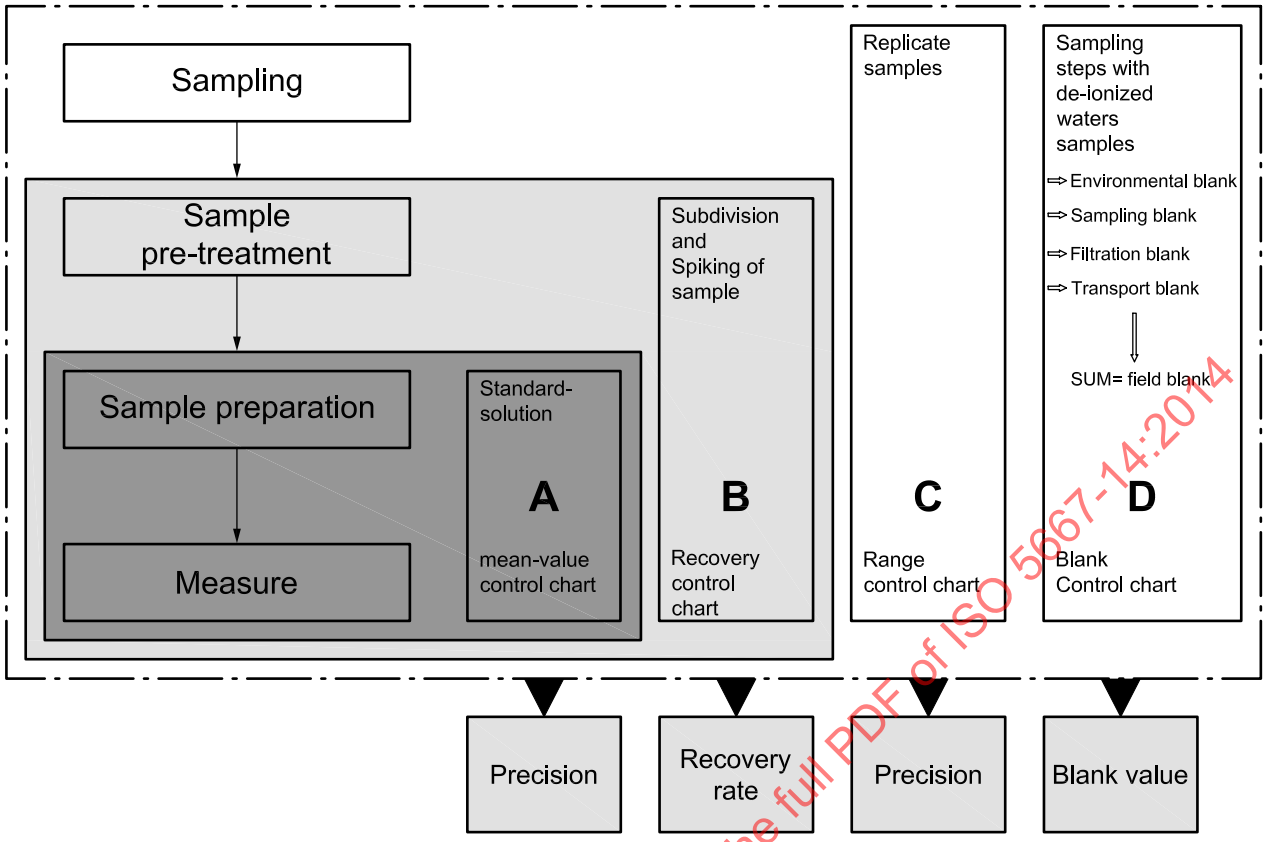
Guidance is given below with respect to quality control procedures, which can be used to identify and quantify the errors associated with sampling.

Quality control measurements are used to control the overall process or part of the analysis steps. Common quality controls are shown in Figure 2.

The accuracy of sampling as the sum of precision and trueness cannot be determined directly, because the inaccuracy of the subsequent steps (sample preparation and measurement) flows into the determination.

The accuracy of the results of the investigation of water from larger quantities in terms of a representative result is usually not verifiable, since the only way to verify the procedure, the spiking normally is not feasible.

The precision of sampling can only be determined indirectly, if the precision of the other sub-steps of the analysis are known.



Key

A Determination of precision and trueness of sample preparation and measurement

B Determination of recovery from sample pre-treatment, sample preparation and measurement

C Determination of precision of the overall process (sampling, sample pre-treatment, sample preparation and measurement)

D Determination of the blank value of the overall process

Figure 2 — Schematic illustration of the usual quality controls for analysis of water[10]

It is important to emphasize that the quality control measures discussed below should ideally be applied in the context of a well-organized approach to quality control. This would include a review of the whole approach to sampling with respect to its fitness for the intended purpose. Within this, the choice of sampling techniques, sampling locations, numbers and types of sample taken, training of sampling staff, sample transport, preservation and storage should be considered. The chosen approach should be adequately documented and a system of record-keeping established. A suitable quality control programme could contain any or all of the techniques listed below. The effort expended on sampling quality control is dependent on the objectives of the programme, but it is recommended that at least 2 % of analytical efforts should be devoted to quality control for sampling. As noted earlier, quality control measures in sampling have three main objectives:

a) to provide a way of monitoring and detecting sampling errors as well as a means of rejecting invalid or misleading data;

b) to act as a demonstration that sampling errors have been controlled adequately; and

c) to indicate the variability of sampling and thereby to give a guide to this important aspect of error. In this clause, the following quality control techniques are described:

   1) the collection of replicate samples as a check on the precision of sampling (see 11.2),

   2) the use of field blank samples to monitor sources of sample contamination (see 11.3), and

3) the use of spiked samples as quality controls to assess sample stability during transport and storage (see 11.6).

11.2 Replicate quality control samples

This term can be used to cover a range of approaches to quality control which aim to assess the random error associated with different levels of the sampling process:

a) *analytical variance*: replicate analyses of the same sample prepared in the laboratory can be used to estimate short-term analytical error;

b) *analytical and subsampling/transport variance*: analyses of replicate samples taken in the field (B_1 and B_2) from the bulk sample (B) (the sample obtained by a single application of the sampling procedure). The difference between such data gives an estimate of analytical plus subsampling/transport variance (includes storage but excludes the effect from sampling containers); and

c) *analytical and total sampling variance*: analysis of bulk samples obtained by separate application of the sampling procedure. This provides an indication of the variance of the whole process of sampling and analysis (A_1 and A_2).

The relationship between the different sampling variances in examples b) and c) is illustrated schematically in Figure 3.

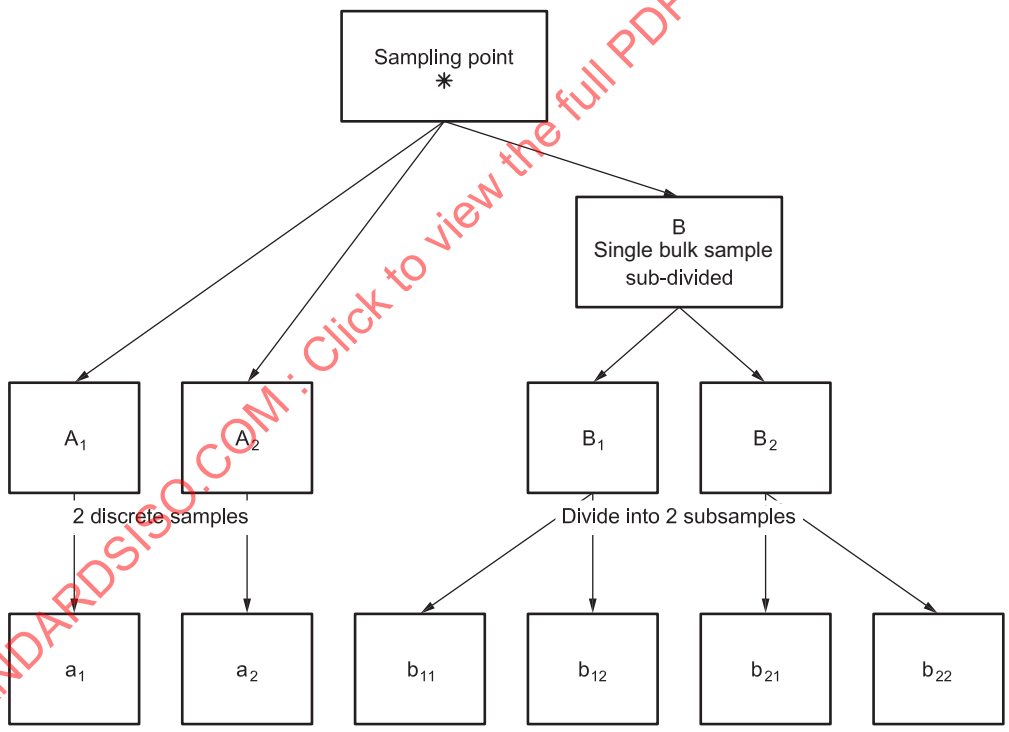


Figure 3 — Flowchart illustrating the relationship between different sampling variances

The difference between A_1 and A_2 gives an estimate of total sampling variance (sampling, containers, storage and analysis).

The difference between B_1 and B_2 (expressed as the mean of b_{11} and b_{12} and b_{21} and b_{22}) gives an estimate of analytical plus sampling variance (including storage, excluding sampling container).

The difference between replicate analyses b_{11} and b_{12}, and b_{21} and b_{22} gives an estimate of analytical precision.

The analysis of replicate samples provides an estimate of the contribution of analytical error for all of the examples in Figures 4 to 9.

A comparison between the different estimates of variance described above can be used to identify the most important sources of measurement uncertainty. This is illustrated in Tables 2 and 3 below.

Table 2 — Analytical variance used to identify sources of measurement uncertainty

Sample No.		1	2	3	4	5	6	7
Duplicate results	–1	1,61	1,72	2,21	1,38	2,25	2,8	1,74
	–2	1,55	1,98	1,99	1,55	2,44	2,55	1,55
Estimate of variance (1 degree of freedom)		0,001 8	0,033 8	0,024 2	0,014 45	0,018 05	0,031 25	0,018 05
NOTE Pooled estimate of variance (the average of the above estimates) with 7 degrees of freedom = 0,020 23.								

The following duplicate results were obtained for a series of waste water samples, each of which was divided into two analytical portions. These were analysed to give the results shown below.

Table 3 — Analytical and subsampling/transport variance for a series of waste water sampling

Sample No.		1	2	3	4	5	6	7
Duplicate results	–1	2,66	1,66	2,31	1,99	1,85	1,81	2,66
	–2	1,85	2,22	1,44	1,55	2,54	2,55	1,85
Estimate of variance (1 degree of freedom)		0,328 1	0,156 8	0,378 5	0,096 8	0,238 1	0,352 8	0,328 1
NOTE 1 Pooled estimate of analytical + sample handling variance — with 6 degrees of freedom = 0,258.								
NOTE 2 The concentrations of the sample chosen should be similar to those chosen in Table 2.								

These two estimates of analytical and analytical and subsampling/transport variance can be compared using an appropriate F-test: observed F value = 12,75.

The F value from the F-Table (for 7 and 6 degrees of freedom and at the 95 % probability level) = 4,2.

The observed F value from the values of Table 2 and Table 3 is larger than the F-Table value hence there is reason to believe that there are important sources of variation at the sampling/handling stage. In the case of samples taken, for example, for the determination of ammonia, it might be reasonable to investigate the possibility that sample preservation might need attention or that concentrations have changed during the period in which the samples were taken.

11.3 Field blank samples

This technique can be used to identify any errors relating to contamination of sampling containers and the sampling process (see Figure 4).

NOTE Field blank samples are laboratory blank samples which are taken into the field, treated as samples and analysed as a check on sampling procedures.

At the laboratory, divide a blank sample of, e.g. de-ionized water into two parts, Part A and Part B. Part A is retained in the laboratory. Part B field blank is transported into the field and subdivided into portions b_1 and b_2.

Portion b_1 should be processed using the sampling container, as far as is practical using the same technique as real samples.

Portion b_2 should be retained and returned to the laboratory without any further processing in the field.

Portion b_1 processed as a real sample, together with the unused portion b_2, should be returned to the laboratory for analysis.

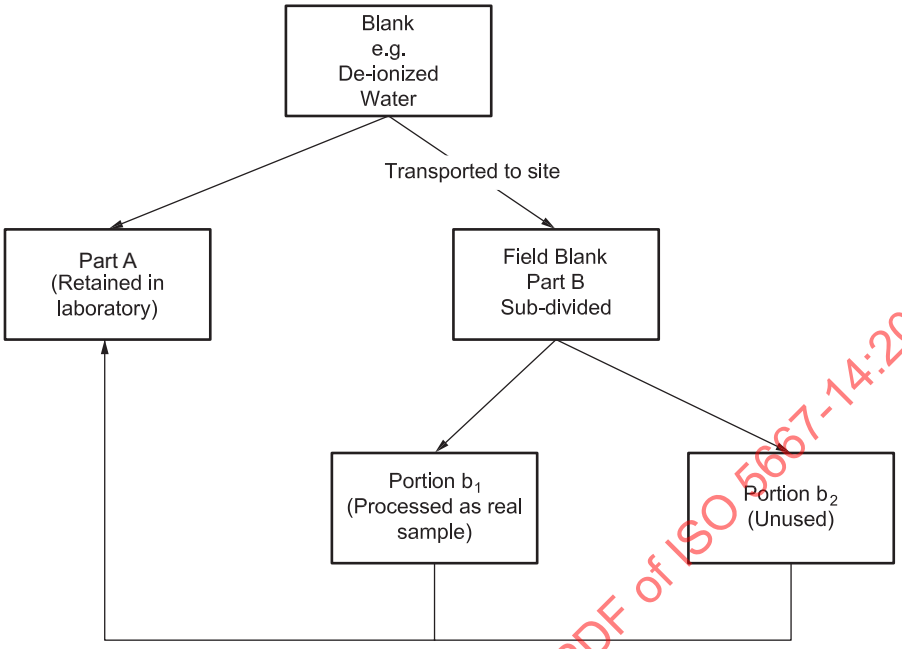


Figure 4 — Flow chart illustrating the field blank samples techniques using de-ionized water to identify sampling contamination errors

The comparison of results of Part A and portion b_1 identifies errors due to sampling, processing and transportation.

The comparison of results of Part A and portion b_2 identifies errors due to sample transportation.

The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers or sampling processes.

11.4 Rinsing of equipment (sampling containers)

This technique can be used to identify any errors relating to contamination of sampling devices and the sampling process caused by incomplete cleaning of the sampling vessels (see Figure 5).

The procedures relating to field blanks can be used on-site immediately after the sampling episode.

At the laboratory, divide a sample of de-ionized water into two parts, Part A and Part B. Part A is retained in the laboratory. Part B (field blank) is transported into the field and subdivided into portions b_1 and b_2.

Portion b_1 should be processed to rinse the sampling container, as far as is practical using the same technique as for real samples.

Portion b_2 should be retained and returned to the laboratory without any further processing in the field. Portion b_1 with the unused portion b_2 should be returned to the laboratory for analysis.

The comparison of results of Part A and the portion b_1 identifies errors due to incomplete cleaning of the sampling vessels.

The comparison of results of Part A and the portion b_2 identifies errors due to sample transportation. The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers or sampling processes due to incomplete cleaning of sampling vessels.

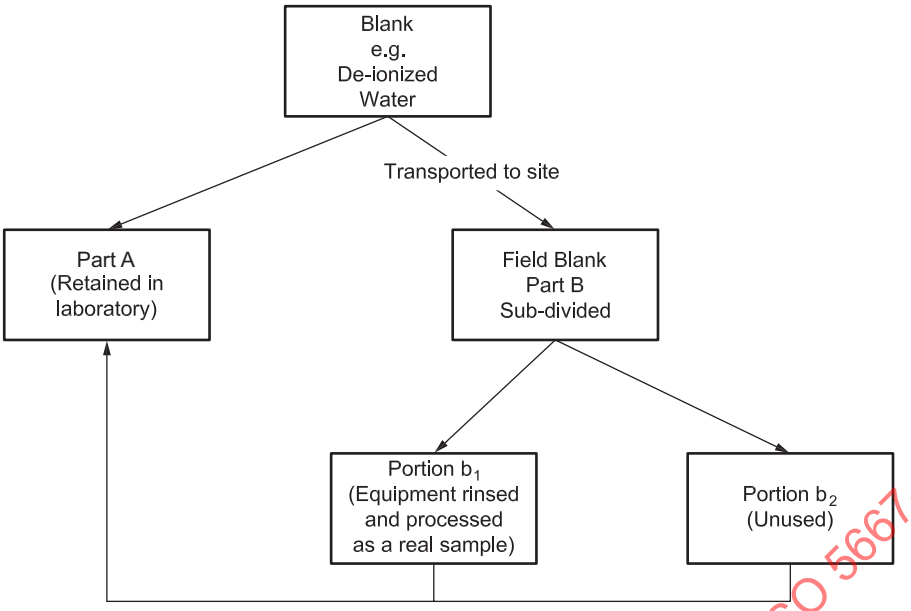


Figure 5 — Flow chart illustrating rinsing using de-ionized water blank to identify cross contamination of sample device and sample processes

11.5 Filtration recovery

11.5.1 General

This technique can be used to identify any errors relating to contamination of sampling containers and the sampling process associated with filtration of samples.

When there is a requirement to filter samples on-site, field blanks and/or standard quality assurance samples should be processed using the same filtering procedures as for real samples.

11.5.2 Filtering of de-ionized water blank

This technique can be used to identify any errors relating to sampling containers, filtration equipment, sampling processes and contamination of the samples (see Figure 6).

At the laboratory, divide a sample of de-ionized water into two parts, Part A and Part B. Part A is retained in the laboratory. Part B (field blank) is transported into the field and subdivided into portions b_1 and b_2.

Portion b_1 should be processed using the sampling container and filtration equipment, as far as is practical using the same technique as real samples. Portion b_2 should be retained and returned to the laboratory without any further processing in the field.

Portion b_1 processed as a real sample, together with the unused portion b_2, should be returned to the laboratory for analysis.

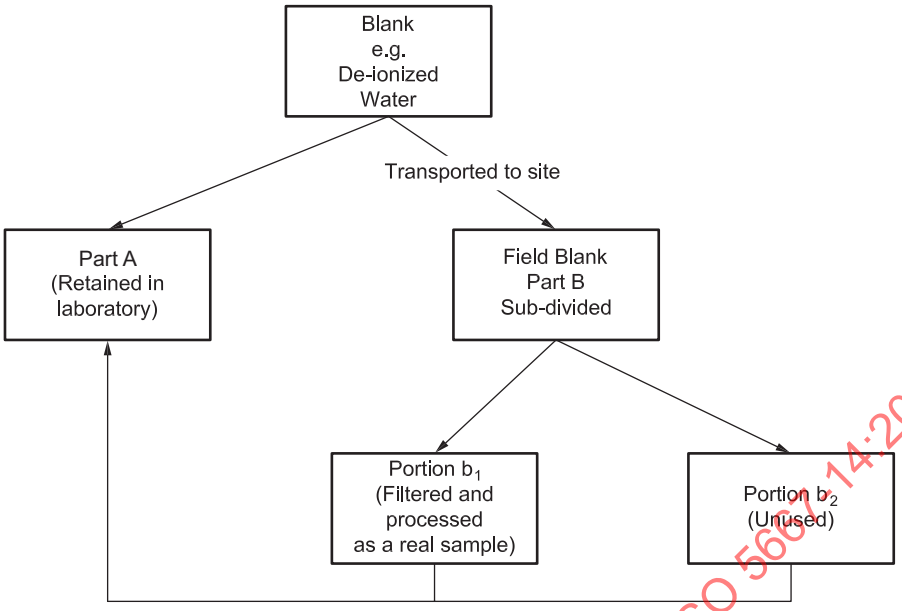


Figure 6 — Flow chart illustrating the filtering of de-ionized water blank technique to identify filtration sample container and process errors

The comparison of results of Part A and the portion b_1 identifies errors due to sampling filtration, processing and transportation.

The comparison of results of Part A and the portion b_2 identifies errors due to sample transportation.

The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers or sampling processes during filtration.

11.5.3 Filtering of spiked quality assurance sample

This technique can be used to identify any errors relating to sampling containers, filtration equipment, sampling processes, and instability and contamination of the samples (see Figure 7).

At the laboratory, prepare a previously analysed environmental sample by spiking the sample with the determinand of interest. The quantity of the determinand in the spike should be chosen so that the measurements are made at the concentration where the best precision is obtained.

Divide this sample into two parts, Part A and Part B. Part A is retained in the laboratory. Part B (Spiked Sample) is transported into the field and subdivided into portions b_1 and b_2.

Portion b_1 should be processed using the sampling container and filtration equipment, as far as is practical using the same technique as for real samples.

Portion b_2 should be retained and returned to the laboratory without any further processing in the field.

Portion b_1 processed as a real sample, together with the unused portion b_2, should be returned to the laboratory for analysis.

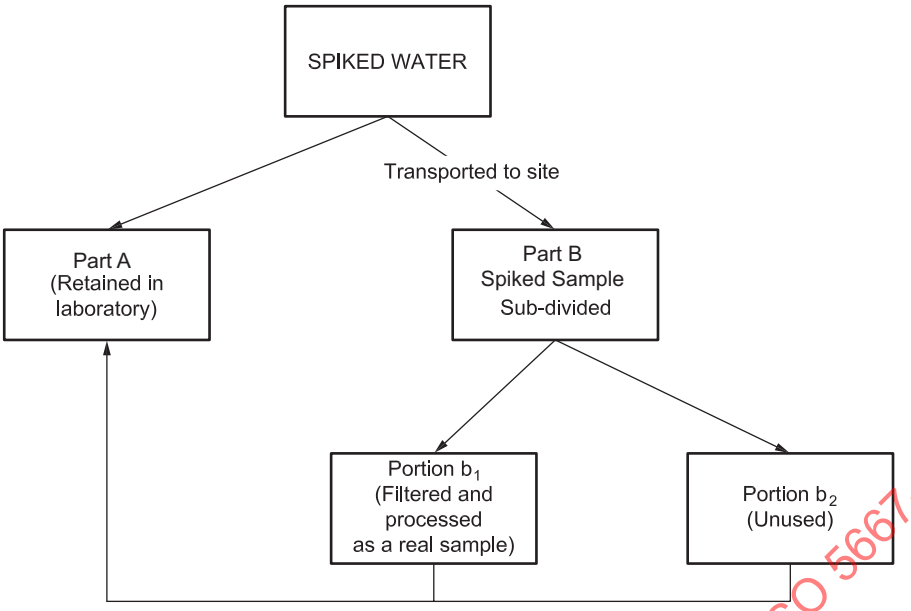


Figure 7 — Flow chart illustrating the filtering of spiked quality assurance sample to identify contamination of samples and sample filtration, and equipment error

The comparison of results of Part A and the portion b_1 identifies errors due to sampling, including sampling processes and filtration equipment, sample instability and transportation.

The comparison of results of Part A and the portion b_2 identifies errors due to sample transportation.

The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers, filtration equipment and sampling processes and errors due to instability and contamination of the sample.

11.6 Technique 1 — Spiked samples

11.6.1 General

This technique can be used for estimating the systematic error of the sampling processes which includes identifying errors relating to contamination of sampling containers and sampling processes. It is particularly valuable in identifying errors due to sample instability, including loss of determinands by volatilization, adsorption and biological factors; for example, determinands such as volatile organic compounds, trace metals (where samples are filtered) and nutrients. There are two main techniques; spiking de-ionized water samples (see Figure 8); and spiking environmental samples (see Figure 9).

11.6.2 Spiked de-ionized water samples

At the laboratory, divide a sample of spiked de-ionized water into two parts, Part A and Part B (field blank). Part A is retained in the laboratory. Part B is transported into the field and subdivided into three portions b_1, b_2, and b_3.

Portion b_1 should be processed using the sampling container, as far as is practical using the same as for real samples.

Portion b_2 should be retained and returned to the laboratory without any further processing in the field.

Portion b_3 should be spiked with a known concentration of the determinand of interest and subdivided into portions b_3(i) and b_3(ii).

Subportion b_3(i) should be processed using the sampling container, as far as is practical using the same technique as real samples.

Subportion b_3(ii) should be retained and returned to the laboratory without any further processing in the field.

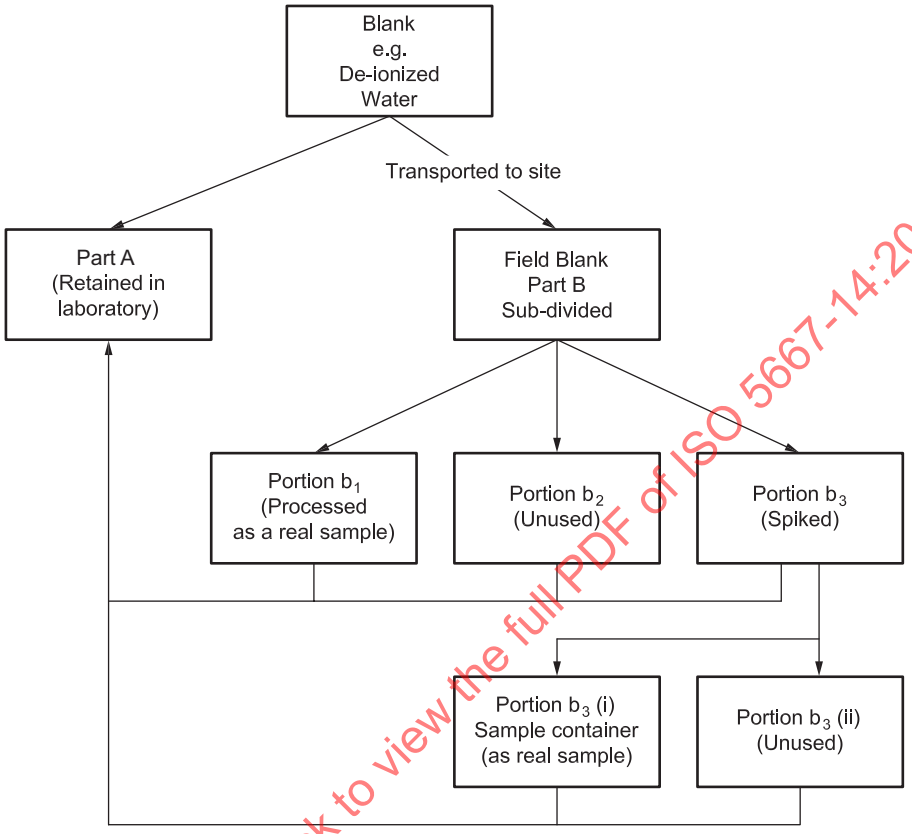


Figure 8 — Flow chart to illustrate Technique 1 spiked de-ionized water samples to identify contamination from sampling container and processes

Return portions b_1, b_2, b_3(i) and b_3(ii) to the laboratory for analysis.

The comparison of results of Part A and the portion b_1 identifies errors due to sampling processing and transportation.

The comparison of results of Part A and the portion b_2 identifies errors due to sample transportation.

The comparison of results of Part A and the spiked portion b_3(ii) identifies errors due to any instability and contamination of the sample and transportation.

The comparison of results of Part A and spiked subportion b_3(i) identifies errors due to sample processing and transportation and any errors due to instability and contamination of the sample.

The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers and sampling processing (eliminates transportation errors).

The comparison of results of portion b_2 and subportion b_3(ii) identifies errors due to instability and contamination of the sample.

The comparison of results of portion b_3(i) and portion b_3(ii) identifies errors due to contamination of sampling containers or sampling processes.

11.7 Technique 2 — Spiked environmental samples

The sample may be prepared either in-laboratory or on-site. Ideally, spiking of samples should be carried out in the field at the time of the sampling. This might require specialist expertise and might be impractical on a routine basis.

Alternatively, prepare at the laboratory a previously analysed environmental sample by spiking the sample with the determinand of interest. The quantity of the determinand in the spike should be chosen so that the measurements are made at the concentration where the best precision is obtained.

Divide this sample into two parts, Part A and Part B. Part A is retained in the laboratory. Part B is transported into the field and subdivided into portions b_1 and b_2.

Portion b_1 should be processed using the sampling container, as far as is practical using the same technique as real samples.

Portion b_2 should be retained and returned to the laboratory without any further processing in the field.

Portion b_1 processed as a real sample together with the unused portion b_2 sample should be returned to the laboratory for analysis.

The comparison of results of Part A and the portion b_1 identifies errors due to sampling processing and transportation.

The comparison of results of Part A and the portion b_2 identifies errors due to sample transportation.

The comparison of results of portion b_1 and portion b_2 identifies errors due to contamination of sampling containers as well as, sampling processes and errors due to instability and contamination of the sample.

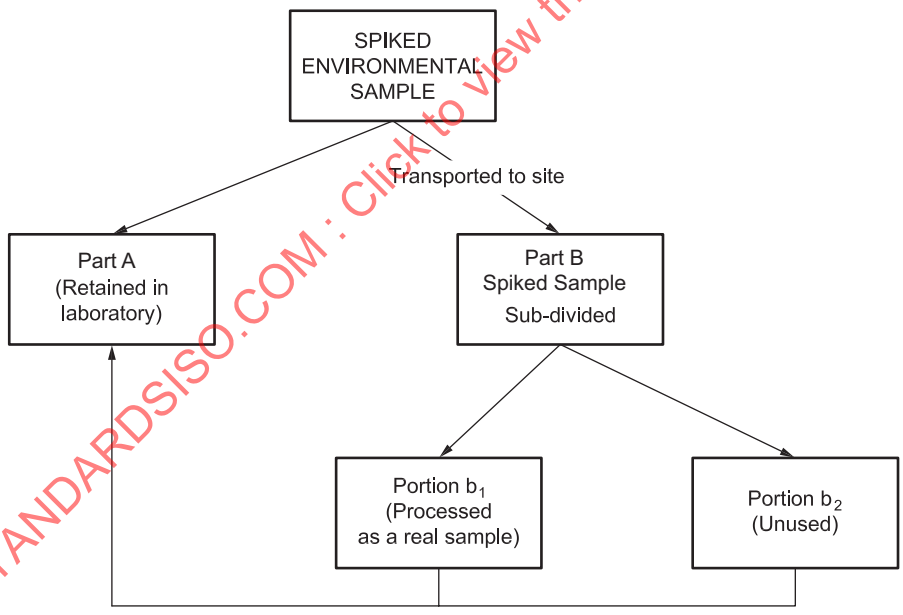


Figure 9 — Flow chart to illustrate Technique 2 spiked environmental samples used to identify contamination from sampling containers and processes

12 Analysis and interpretation of quality control data

12.1 Shewhart control charts

The aim of the quality control system is to ensure that the reliability of the sampling data are consistent with the performance criteria required.

The most widely used form of control chart is the Shewhart chart (see ISO 7870-2). This takes the form of a chart on which the variable of interest is plotted sequentially. The measured values are compared with the control value. Much information can be gained merely by a visual examination of the chart (see Figures B.1 and B.2).

12.2 Construction of duplicate control charts

This takes the form of a chart on which the difference, d, between duplicate determinations is plotted.

$$d = R_1 - R_2 \quad (1)$$

where

R_1 is the result of the first sample analysed;

R_2 is the result of the second sample analysed.

It is essential always to subtract the second result from the first and plot the difference with due regard to its sign. The expected value for the chart is zero. The relevant sample standard deviation, s_d, is calculated from:

$$s_d = \sqrt{\sum_{i=1}^{m} \frac{\left(d_i - \bar{D}\right)^2}{m-1}} \quad (2)$$

where

$\bar{D}$ is the mean difference between duplicates over m batches of samples

d_i are individual differences

m is the number of pairs of duplicates

Examples of a control chart for duplicate data and recovery are given in Annex B.

13 Independent audits

It is recommended that sampling quality programmes include regular independent reviews. See ISO/IEC 17025 and ISO 19011.

The reviews should include but not be restricted to the following evaluations.

a) Do the sampling personnel have clearly defined responsibilities, appropriate qualifications, appropriate training and adequate supervision?

b) Are sample collection locations appropriately chosen and prepared?

c) Are there any safety concerns? Do sampling personnel have the experience and training to handle these types of safety issues?

d) Is the sampling and monitoring equipment regularly serviced, maintained and calibrated?

e) Are all reagents clearly labelled and not past expiry date? Do staff wear necessary safety clothing, glasses and equipment? Do staff dispose of old reagents and used material safely and appropriately?

f) Can sampling personnel recognize degraded reagents or unusual samples?

g) Does each member of staff have an up-to-date sampling manual and follow the specified methods? Have all methods been documented and verified?

h) Are samples correctly labelled, handled, preserved and transported to the laboratory appropriately and within target limits?

i) Are sample collection records completed and do they unambiguously identify sample location, sample time and name of the person taking the sample? Also, do they include analytical methods and associated quality control and quality assurance for measurements made on-site?

j) If sampling staff are responsible for servicing online monitoring equipment, are the necessary maintenance and quality verification documents regularly updated?

k) Are the sample collection records and data safely archived and readily retrievable?

Annex A
(informative)

Common sources of sampling error[7]

A.1 General error

General sources of error include:

a) confusion of sampling collection location by, for example, inadequate documentation (see 6.2, 7.2 and 9);

b) confusion of samples due to inadequate labelling or incomplete or incorrectly completed Sampling protocols (see Clauses 8 and 9);

c) sampling of non-representative, inhomogeneous or other inappropriate sampling points, not conforming to the research question, e.g. by formulating an inadequate sampling order (see Clause 6);

d) inadequate or incomplete sample handling on-site, during transport and storage (see 7.4 and Clause 10).

A.2 Contamination by import of substances in the sample

Sources of error in this category include:

a) carry over of substances by inadequate rinsing/cleaning of sampling equipment (see 5.4, 7.1 and 7.2);

b) contamination of the sample by using unsuitable sampling devices (e.g. abrasion of material, lubricant in pumps) and sample containers (see 5.4 and Clause 7);

c) import of contaminants during sampling procedure, e.g. abrasion of bridge railings, bank material, sediment (see 7.2 and 7.4);

d) risk of cross contamination from preservative chemicals (see 7.4.6);

e) confusion of closures (7.1);

f) use of unsuitable or not sufficiently purified facilities on-site, e.g. pipettes, filtration equipment (see 7.2 and 7.4);

g) contamination from the environment, for example, by

   1) soil contact of sampling devices, tubes, sample containers and closures (see 7.4.1 and 7.4.6),

   2) the use of contaminated sampling equipment (see 7.2 and 7.4.2), and

   3) filling and storing of samples in air contaminated with pollutants such as exhaust fumes, outgassing of preservatives or strongly contaminated samples (see 7.4.1, 7.4.6 and Clause 10).

A.3 Loss by export of pollutants from the sample

Sources of error in this category include:

a) outgassing of volatile substances by storing it in non-gas-tight or incompletely filled sample containers (see 7.4.1 and 7.4.2);

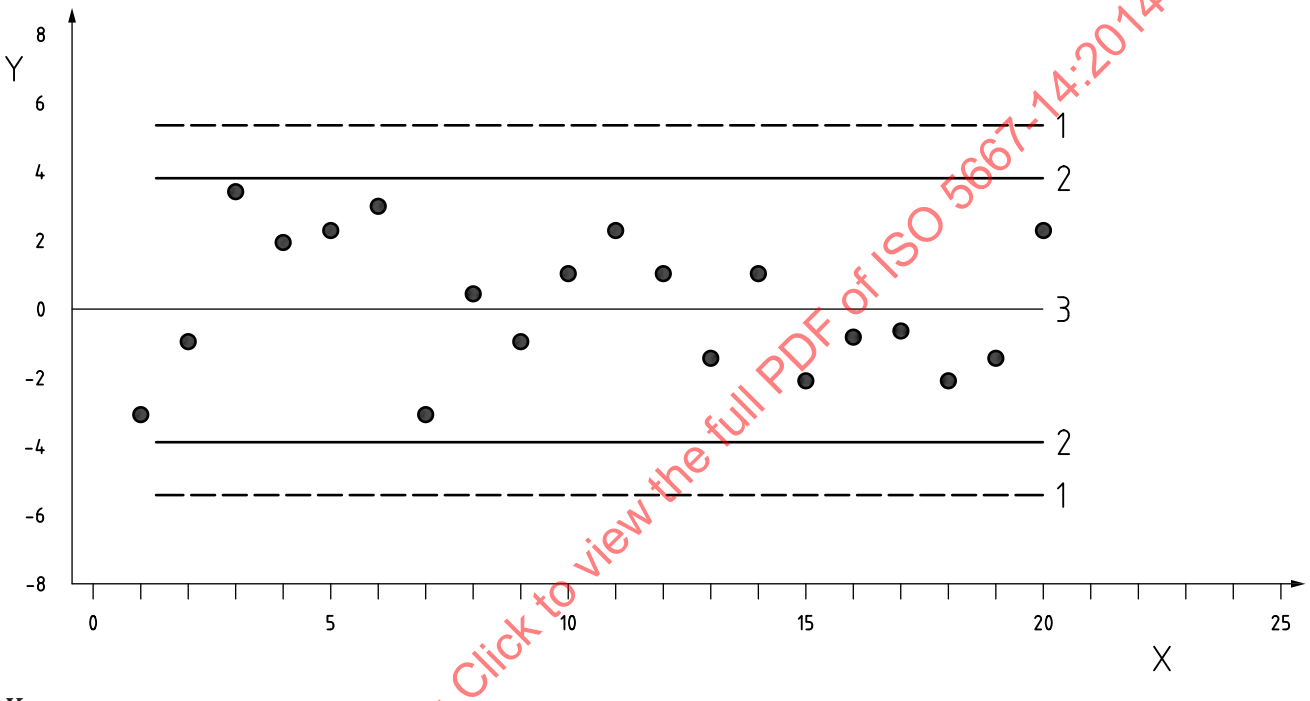
b) losses of materials due to incorrectly applied sampling or filling technology, e.g. use of suction pumps, multiple transfer or turbulent filling of sample (see 7.4.1, 7.4.2 and 7.4.4);

c) diffusion of sample constituents in and/or sorption on tube and container materials (see 7.4.2).

Annex B
(informative)

Control charts

B.1 Example of a control chart for duplicate data (Figure B.1)



Key

X control sample number
Y difference in value
1 action limit
2 warning limit
3 mean

Figure B.1 — Shewhart chart for duplicate control samples

Suspended solids are determined in a range of industrial effluents to monitor compliance with a discharge limit of 30 mg/l.

A series of duplicate samples, examples as shown in Figure B.1, have been taken for effluent samples of suspended solids concentrations in the range of interest 20 mg/l to 40 mg/l. It is assumed that the standard deviation of sampling and analysis is constant across this restricted range. This will allow the precision of sampling to be estimated and checked on a routine basis.

In each case, a single bulk sample of effluent was taken and thoroughly homogenized. The bulk sample was then sub-sampled using the routine sampling procedure to produce duplicate test samples. Each of these test samples was analysed once.

Analytical data for 20 duplicate samples are shown in Table B.1.