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Water quality — Sampling —

Part 14:
Guidance on quality assurance 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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Content

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Foreword

ISO (the International Organization for Standardization) is a world-wide 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.

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.

International Standard ISO 5667-14 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 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*

— *Part 2: Guidance on sampling techniques*

— *Part 3: Guidance on the preservation and handling of 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, wastewater and related sludges*

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

Annexes A and B of this part of ISO 5667 are for information only.

Introduction

Quality control procedures are required 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;

d) to provide information on suitably abbreviated quality assurance procedures that may 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, 2 and 3.

The general terminology is in accordance with that published in ISO/TC 147, *Water quality*, and more particularly with the terminology on sampling given in ISO 6107-2.

Water quality — Sampling —

Part 14:
Guidance on quality assurance 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 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 in some circumstances may be applicable to sludge and sediment sampling.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 5667. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 5667 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

3 Definitions

For the purposes of this part of ISO 5667, the following definitions apply.

3.1
accuracy
closeness of agreement between a test result and the accepted reference value

[ISO 3534-1]

NOTE The term accuracy, when applied to a set of test results, involves a combination of random and systematic error or bias components.

3.2
bias
difference between the expectation of the test results and an accepted reference value

[ISO 3534-1]

NOTE 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 accepted reference value is reflected by a larger bias value.

3.3
precision

closeness of agreement between independent results obtained under stipulated conditions

[ISO 3534-1]

NOTE 1 The variation associated with test results from repeated sampling operations will be subject to variation from analytical sources as well as from sources connected with the sampling process. A comparison of random error from repeated sampling operations with that from repeated analysis of the same sample can be used to deduce the contribution of sampling to overall random error.

NOTE 2 Precision depends only on the distribution of random errors and does not relate to the true value or the specified value, (ISO 3534-1). The measure of precision is expressed in terms of a standard deviation value. Improved precision is reflected in a smaller standard deviation value.

NOTE 3 The ‘independence’ of test results reflects the extent to which results are obtained in a manner not influenced by any previous result on the same test object (ISO 3534-1). Quantitative measures of precision depend critically on stipulated conditions. The well-known terms ‘repeatability’ and ‘reproducibility’ relate to specific types of stipulated conditions. The former term corresponds to measurements made under the same controlled (same method, strictly adhered to in the same laboratory) conditions; the latter term refers to the same method used in different laboratories.

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
comparability

degree of agreement with respect to control over random and systematic errors

3.6
Certified Reference Material
CRM

stable, homogeneous material, with a composition closely matching that of the sample to be analysed, for which the concentrations of the determinands of interest in that material are known with a known degree of uncertainty

NOTE In most chemical analyses the traceability of measurement can be obtained by a series of calibrations that demonstrates that no loss of determinand or contamination occurs during the sample treatment. This traceability can be based on the analysis of a CRM.

3.7
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 Field blank samples are laboratory blank samples which are taken into the field, treated as samples and analysed as a check on sampling procedures.

[ISO/TR 13530]

3.8
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

[ISO/TR 13530]

3.9
recovery

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

NOTE Recovery is calculated from the difference between results obtained from a spiked and an unspiked aliquot of sample and is usually expressed as a percentage.

[ISO/TR 13530]

3.10
control chart

chart, with upper and lower control limits, on which values of some statistical measure for a series of samples, spiked samples and blanks, are plotted, usually in date or sample number order

NOTE 1 The chart frequently shows a central line to assist detection of a trend of plotted values toward either control limit.

[ISO 3534-2]

NOTE 2 In some control charts, the control limits are based on the within-batch data plotted on the chart; in others, the control limits are based on adopted standard or specified values applicable to the statistical measures used.

NOTE 3 The cumulative sum (cusum) chart is a type of control chart. Cusum charts are used for detecting small permanent shifts in trends that may remain undetected when using the Shewhart control chart. The basic principle of the most common type of cusum chart is based on the plotted value, which is the cumulative sum of deviations of successive sample statistics from a target value. When a process change is made, the sum is returned to zero. The ordinate of each plotted point represents the algebraic sum of the previous ordinate and the most recent deviation from the target.

Cusum charts are generally interpreted by masks superimposed on the chart, a signal occurring if the path of the cusum intersects or touches the boundary of the mask (ISO 3534-2).

3.11
Shewhart control chart

control chart to show if a process is in statistical control

[ISO 3534-2 and ISO 8258]

NOTE It may be a chart using attributes (for example, proportion nonconforming) for evaluating a process, or it may be a chart using variables (for example, average and range) for evaluating a process. Examples are:

- X-bar chart - the sample means are plotted in order to control the mean value of a variable.;
- R chart - the sample ranges are plotted in order to control the variability of a variable;
- s chart - the sample standard deviations are plotted in order to control the variability of a variable;
- s^2 chart - the sample variances are plotted in order to control the variability of a variable;
- C chart - the number of defectives (per batch, per day, per machine, etc.) is plotted.

3.12
action control upper [lower] limit

limit above [below] which, or the limits outside which, the statistic under consideration lies when action should be taken

[ISO 3534-2]

NOTE 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 may be present and that action may be required to identify and reduce them.

3.13
warning control upper [lower] limit

limit below [above] which (upper [lower] limit), or the limits between which, the statistic under consideration lies with a high probability when the process is under control

[ISO 3534-2]

NOTE 1 When the value of the statistic computed from a sample is outside the warning limits but inside the action limits, increased supervision of the process is generally necessary and rules may be applied for action in particular processes.

NOTE 2 At the warning limits, attention is called to the possibility of out-of-control conditions, but further action is not necessarily required.

NOTE 3 The warning limits will always be within the action limits.

NOTE 4 Warning limits are usually set so that only 5 % of results should normally fall outside them. Under certain circumstances, successive results outside warning limits indicate that assignable causes of variation are present and that actions are required to identify and reduce errors.

NOTE 5 The limits are calculated from the standard deviation of the statistic under consideration of at least 20 samples. Warning and action control limits are applied to individual sampling results.

3.14
central line

line on a control chart representing the long-term average or a prespecified value of the statistical measure being plotted

[ISO 3534-2]

4 Sources of sampling error

Sources of error 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 affect 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, may be a source of error.

e) Sampling from nonhomogenized water bodies

f) Sample transportation (see clause 6).

5 Sampling quality control techniques

5.1 General

Sampling is defined in ISO 5667-2 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 errors associated with sampling.

A complete overview of quality assurance applied to sampling is outside the scope of this document. However, 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 and hence 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.

The following quality control techniques are described below.

- the collection of replicate samples as a check on the precision of sampling;
- the use of field blank samples to monitor sources of sample contamination;
- the use of spiked samples as quality controls to assess sample stability during transport and storage.

5.2 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 + 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 sampling variance (includes storage but excludes the effect from sampling containers).

c) analytical + 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 1.

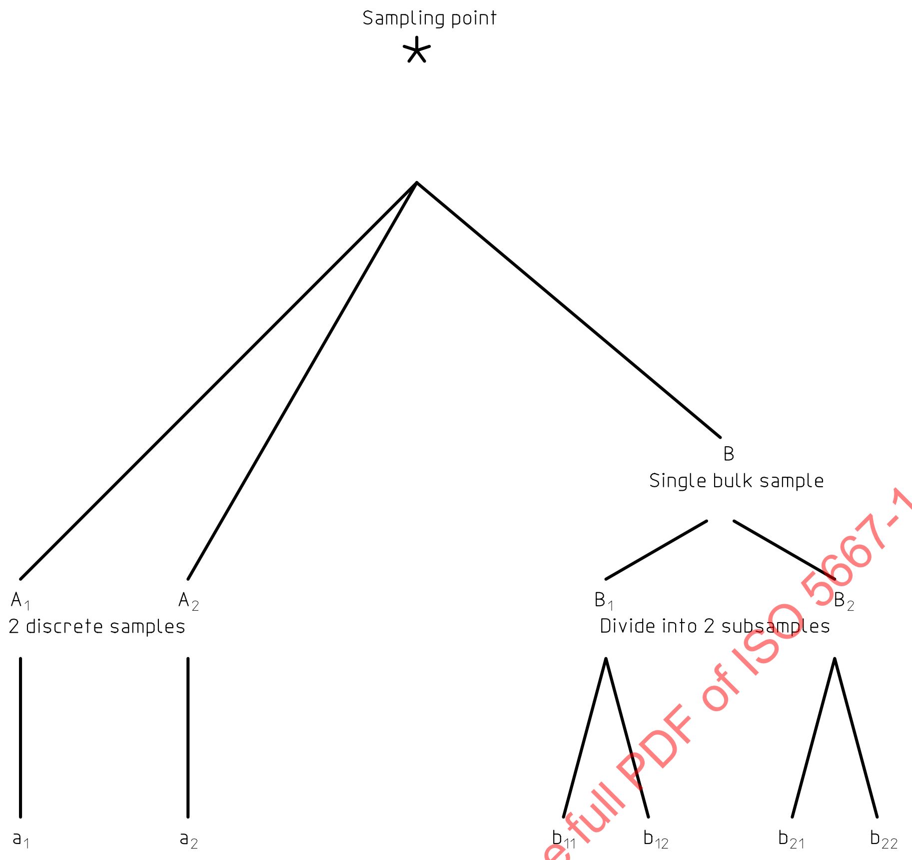

Figure 1 — Relationship between different sampling variances

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} & b_{12} and b_{21} & b_{22}) gives an estimate of analytical plus sampling variance (including storage, excluding sampling container).

The difference between replicate analyses b_{11} & b_{12} and b_{21} & 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 2 to 7.

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 1 and 2 below.

Table 1 — Analytical variance

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 wastewater samples, each of which was divided into two analytical portions. These were analysed to give the results shown below.

Table 2 — Analytical + subsampling/transport variance

Sample No.	1	2	3	4	5	6
Duplicate results -1	2,66	1,66	2,31	1,99	1,85	1,81
-2	1,85	2,22	1,44	1,55	2,54	2,65
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

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 1.

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

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

The observed F value is larger than the table 1 and table 2 values — 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 may need attention or that concentrations have changed during the period in which the samples were taken.

5.3 Field blank samples

This technique can be used to identify any errors relating to contamination of sampling containers and the sampling process (see figure 2).

At the laboratory, divide a sample of deionized water 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, should be returned to the laboratory for analysis.

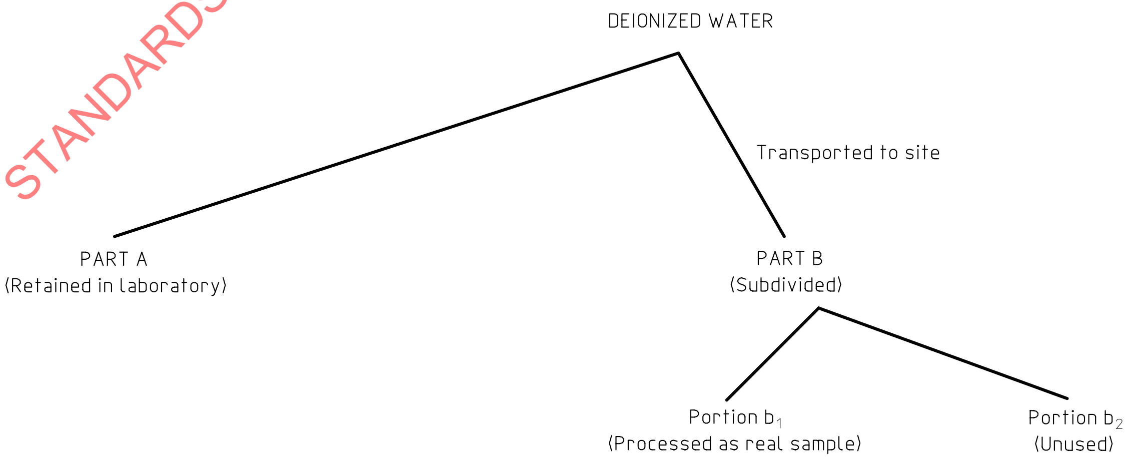

Figure 2 — Field blank samples using deionized water

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 or sampling processes.

5.4 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 3).

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

At the laboratory, divide a sample of deionized water 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 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.

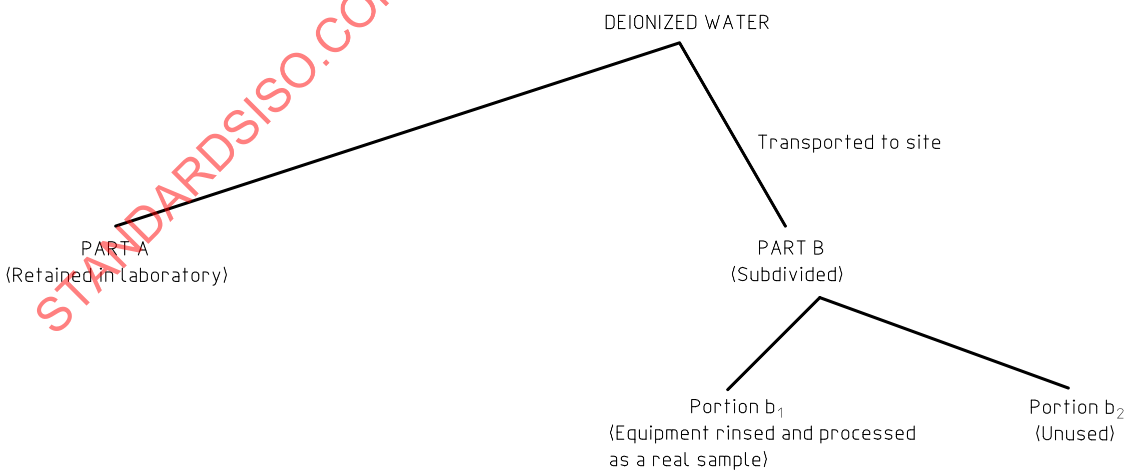

Figure 3 — Rinsing using deionized water blank

5.5 Filtration recovery

5.5.1 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, then field blanks and/or standard quality assurance samples should be processed using the same filtering procedures as for real samples.

5.5.2 Filtering of deionized 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 4).

At the laboratory, divide a sample of deionized water 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 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.

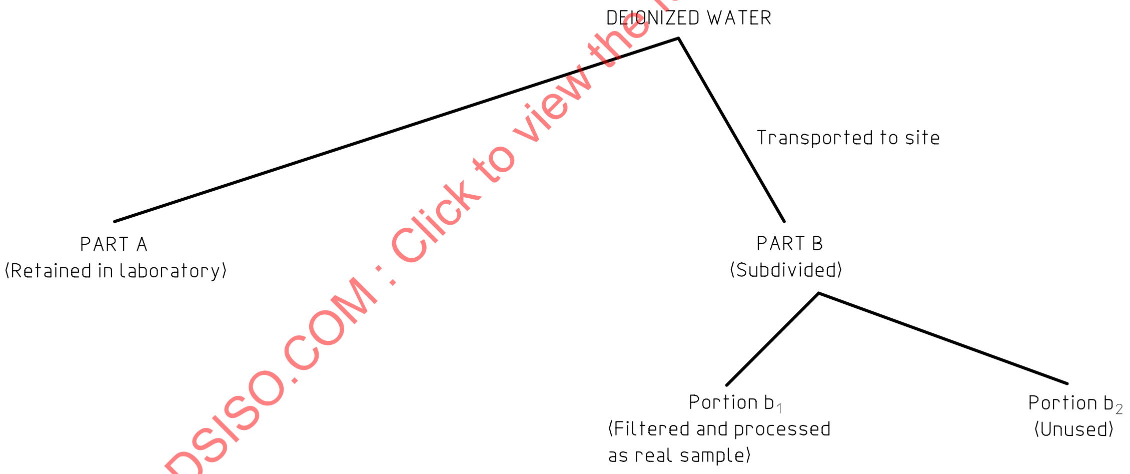

Figure 4 — Filtering of deionized water blank

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.

5.5.3 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 5).

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 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.

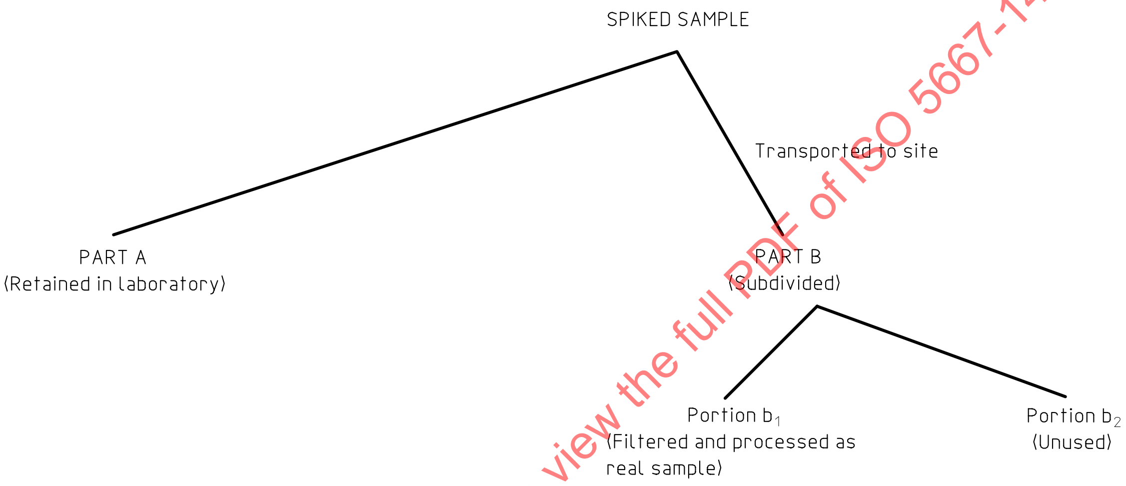

Figure 5 — Filtering of spiked quality assurance sample

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.

5.6 Spiked samples

5.6.1 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, 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 deionized water samples (see figure 6) and spiking environmental samples (see figure 7).

5.6.2 Spiked deionized water samples

At the laboratory, divide a sample of spiked deionized water 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 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.

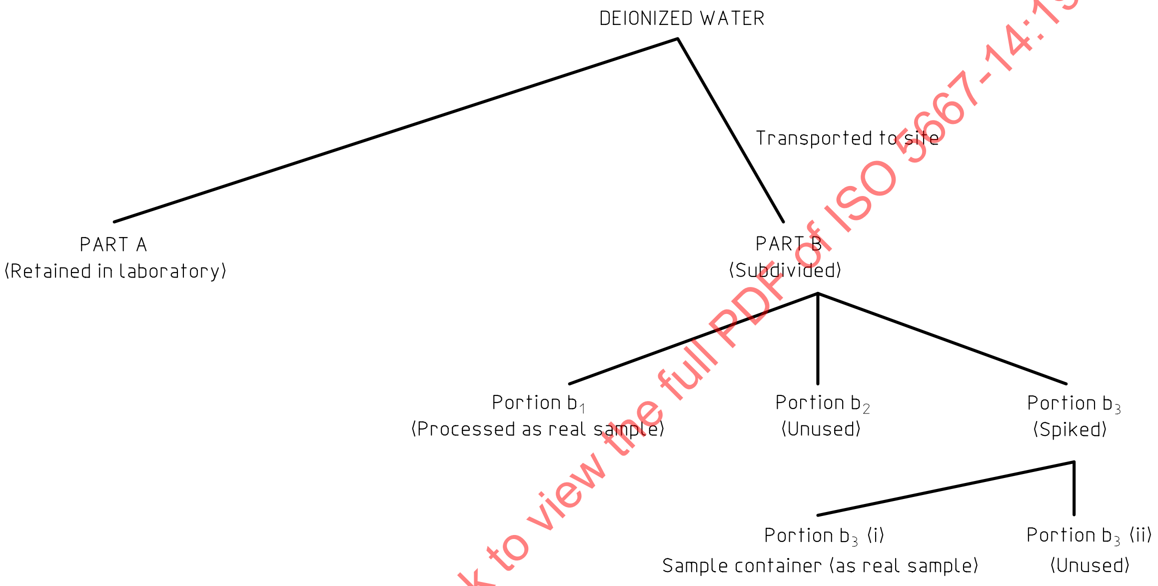

Figure 6 — Spiked deionized water samples

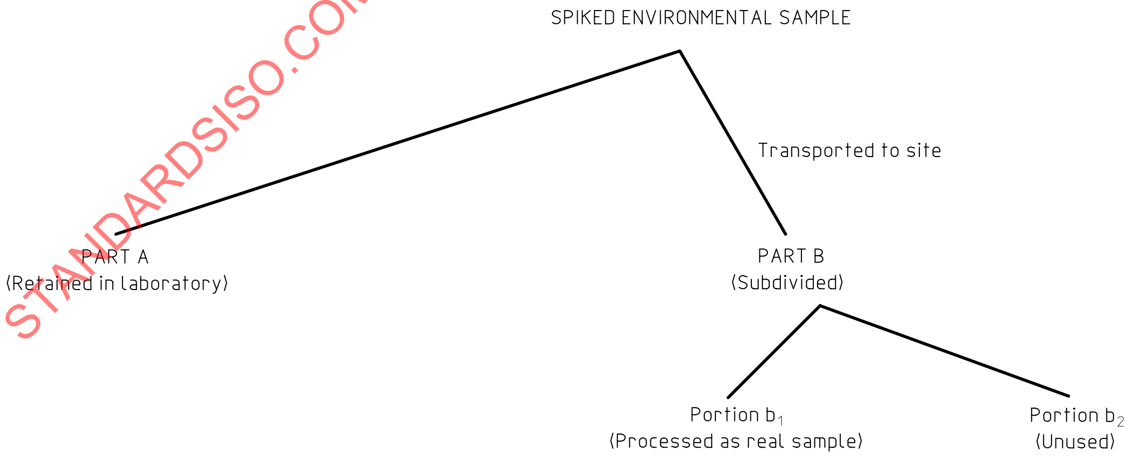

Figure 7 — Spiked environmental samples

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 sub portion 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 sub portion b_3(ii) identifies errors due 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.

5.6.3 Spiked environmental samples

Ideally, spiking of samples should be carried out in the field at the time of the sampling. This may require specialist expertise and may 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 and sampling processes and errors due to instability and contamination of the sample.

6 Transport, stabilization and storage of samples

Reference should be made to ISO 5667-3 for guidance on sample handling and preservation. Care is essential to ensure that any preservatives are accurately prepared and dispensed. 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.

Ensure that sample containers are delivered to the laboratory as routine samples. It is recommended that sample containers are tightly sealed and protected from the effects of light and excessive heat, because the characteristics of the sample may rapidly deteriorate due to gas exchange, chemical reactions and the metabolism of organisms which may be present. Ensure that samples which cannot be analysed quickly are stabilized. Cooling to 4 °C may be applied; for longer periods, freezing to −20 °C as recommended in ISO 5667-3. In the latter case, ensure that the sample is completely thawed before use, as the freezing process may have the effect of concentrating some components in the inner part of the sample which freezes last. Samples may be preserved by the addition of chemicals of suitable quality. Ensure that the chosen method of preservation does not interfere with the subsequent examination or influence the results. Record all preservation steps in the test report.

NOTE Quality assurance samples used for transportation, stabilization and storage should be treated to the same processes as test samples.

7 Analysis and interpretation of quality control data

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

7.1 Shewhart control charts

The most widely used form of control chart is the Shewhart chart (see ISO 8258). 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 A.1 and A.2.)

7.2 Construction of duplicate control charts

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

$$d = R1 - R2,$$

where

$R1$ is the result of the first sample analysed;

$R2$ 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:

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

where

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

d_i are individual differences.

Examples of a control chart for duplicate data and recovery are given in annex A.

8 Sample identification and records

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.

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

Annex A
(informative)

Control charts

A.1 Example of a control chart for duplicate data (figure A.1)

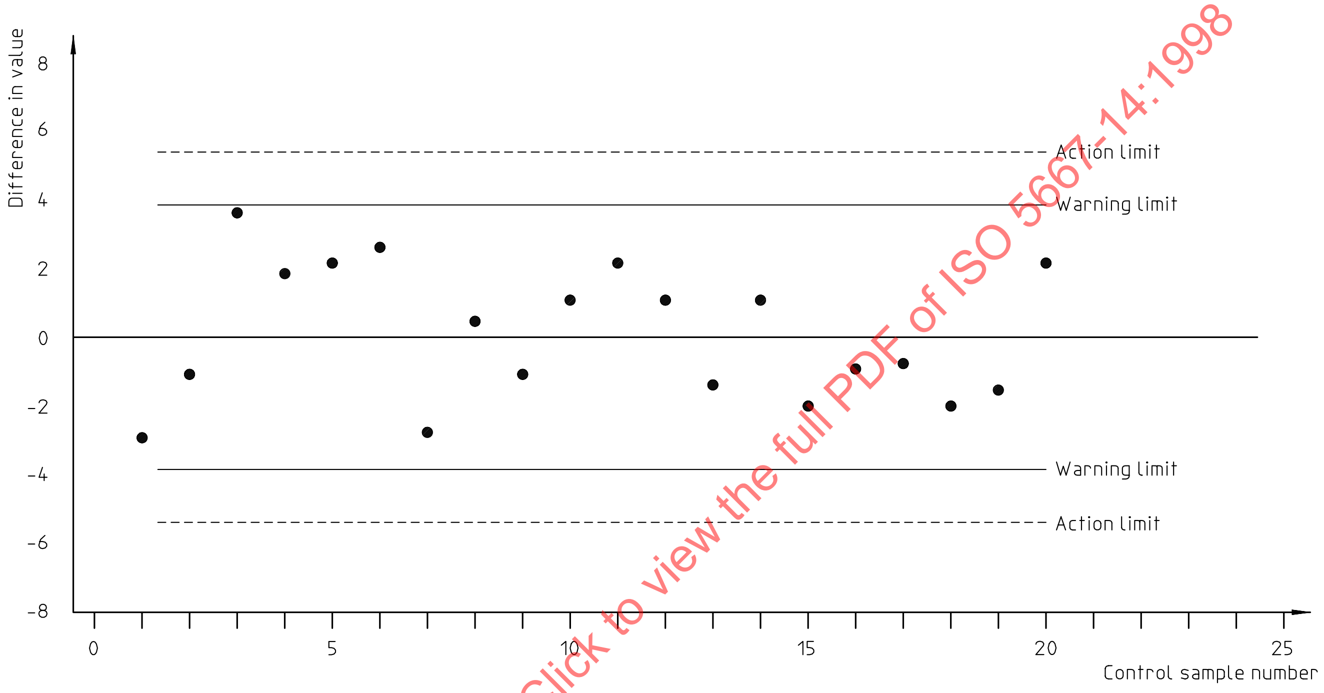

Figure A.1 — Shewhart chart for duplicate control samples

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 A.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 subsampled 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 A.1.

The corresponding control chart is attached. The central value of the chart is fixed at the mean value of the differences between duplicate data. The action and warning limits are drawn at ± 3 and ± 2 standard deviations, respectively.

Table A.1 — Suspended solids data for quality control duplicate samples

Measured values mg/l		**Difference** mg/l
1st	**2nd**	
33,2	36,0	– 2,8
25,6	26,2	– 0,6
38,2	34,8	3,4
28,8	27,2	1,6
31,4	29,8	1,6
34,6	32,2	2,4
22,4	24,6	– 2,2
27,2	26,8	0,4
22,0	23,2	– 1,2
34,0	32,8	1,2
24,6	22,6	2,0
23,8	23,0	0,8
33,6	35,2	– 1,6
37,4	36,6	0,8
29,2	31,4	– 2,2
30,0	31,2	– 1,2
36,4	35,8	0,6
37,2	39,4	– 2,2
33,6	35,0	– 1,4
28,0	26,4	1,6
Mean difference		1,0
Standard deviation of differences		0,471 8
NOTE The observed standard deviation reflects analytical precision as well as that of sampling.		

A.2 Example of a control chart for recovery (figure A.2)

The data below (see table A.2) relate to the determination of trace concentrations of mercury in river waters. For each batch of analysis a spiking recovery test was carried out by analysing a river sample before and after spiking with 90 ng/l. The details of spiking were as follows:

C = Concentration of spiking solution = 100 µg/l

V = Volume of sample taken = 1 998,2 ml

W = Volume of spike = 1,8 ml

S = Measured concentration in the spiked sample (see below)

U = Measured concentration in the unspiked sample (see below)

Percentage recovery is calculated as:

$$\% \text{ Recovery} = 100 \cdot [S \cdot (V + W) - U \cdot V]/C \cdot W \qquad (2)$$