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Water quality — Sampling —

Part 3:
Preservation and handling of water samples

Qualité de l’eau — Ėchantillonnage —

Partie 3: Conservation et la manipulation des échantillons d’eau

Reference number
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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 5667-3 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 6, *Sampling (general methods)*.

This fourth edition cancels and replaces the third edition (ISO 5667-3:2003), 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 and sampling techniques*
- *Part 3: Preservation and handling of water samples*
- *Part 4: Guidance on sampling from lakes, natural and man-made*
- *Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems*
- *Part 6: Guidance on sampling of rivers and streams*
- *Part 7: Guidance on sampling of water and steam in boiler plants*
- *Part 8: Guidance on the sampling of wet deposition*
- *Part 9: Guidance on sampling from marine waters*
- *Part 10: Guidance on sampling of waste waters*
- *Part 11: Guidance on sampling of groundwaters*
- *Part 12: Guidance on sampling of bottom sediments*
- *Part 13: Guidance on sampling of sludges*
- *Part 14: Guidance on quality assurance of environmental water-sampling and handling*
- *Part 15: Guidance on the preservation and handling of sludge and sediment samples*
- *Part 16: Guidance on biotesting of samples*
- *Part 17: Guidance on sampling of bulk suspended solids*
- *Part 19: Guidance on sampling of marine sediments*

- *Part 20: Guidance on the use of sampling data for decision making — Compliance with thresholds and classification systems*
- *Part 21: Guidance on sampling of drinking water distributed by tankers or means other than distribution pipes*
- *Part 22: Guidance on the design and installation of groundwater monitoring points*
- *Part 23: Guidance on passive sampling in surface waters*

Introduction

This part of ISO 5667 is intended to be used in conjunction with ISO 5667-1, which deals with the design of sampling programmes and sampling techniques.

Where possible this part of ISO 5667 has been brought into line with current standards. Where new research or validation results have provided new insights, the latest knowledge has been used.

Guidance on validation protocols can be found in ISO Guide 34.[63]

Water quality — Sampling —

Part 3:
Preservation and handling of water samples

NOTICE — This part of ISO 5667 and the analytical International Standards listed in Annex A are complementary. Where no analytical International Standard is applicable, the technique(s) described in Tables A.1 to A.3 take(s) normative status.

When new or revised analytical standards are developed with storage times or preservative techniques differing from those in Tables A.1 to A.3, then the storage times or preservative techniques should be validated and presented to ISO/TC 147/SC 6/WG 3 for incorporation into the next revision of this part of ISO 5667.

1 Scope

This part of ISO 5667 establishes general requirements for sampling, preservation, handling, transport and storage of all water samples including those for biological analyses. It is not applicable to water samples intended for microbiological analyses as specified in ISO 19458, ecotoxicological assays, biological assays, and passive sampling as specified in the scope of ISO 5667-23.

This part of ISO 5667 is particularly appropriate when spot or composite samples cannot be analysed on site and have to be transported to a laboratory for analysis.

2 Normative references

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667 (all parts), *Water quality — Sampling*

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

3 Terms and definitions

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

3.1
integrity
property that the parameter(s) of interest, information or content of the sample container has not been altered or lost in an unauthorized manner or subject to loss of representativeness

3.2
sample preservation
any procedure used to stabilize a sample in such a way that the properties under examination are maintained stable from the collection step until preparation for analysis

[ISO 11074:2005,[29] 4.4.20]

NOTE Different analytes may require several samples from the same source that are stabilized by different procedures.

3.3

sample storage

process, and the result, of keeping a sample available under predefined conditions for a (usually) specified time interval between collection and further treatment of a sample

NOTE 1 Adapted from ISO 11074:2005,[29] 4.4.22.

NOTE 2 Specified time is the maximum time interval.

3.4

storage time

period of time between filling of the sample container and further treatment of the sample in the laboratory, if stored under predefined conditions

NOTE 1 Sampling finishes as soon as the sample container has been filled with the sample. Storage time ends when the sample is taken by the analyst to start sample preparation prior to analysis.

NOTE 2 Further treatment is, for most analytes, a solvent extraction or acid destruction. The initial steps of sample preparation can be steps complementary to the storage conditions for the maintenance of analyte concentrations.

4 Sampling and chain of custody

If there is a need to take samples, this is done according to a sampling programme. The first step is to design a sampling programme. Guidance on this topic is given in ISO 5667-1.

Depending on the sample type and matrix, the guidelines found in the relevant part(s) of ISO 5667 and ISO 19458 shall be consulted.

The process of preservation and handling of water samples consists of several steps. During this process, the responsibility for the samples might change. To ensure the integrity of the samples, all steps involving the sample shall be documented.

All preparation procedures shall be checked to ensure positive or negative interferences do not occur. As a minimum, this shall include the analysis of blanks (e.g. field blank or sample container) or samples containing known levels of relevant analytes as specified in ISO 5667-14.

5 Reagents and materials

WARNING — Certain preservatives (e.g. acids, alkalis, formaldehyde) need to be used with caution. Sampling personnel should be warned of potential dangers, and appropriate safety procedures should be followed.

The following reagents are used for the sample preservation and shall only be prepared according to individual sampling requirements. All reagents used shall be of at least analytical reagent grade and water shall be of at least ISO 3696, grade 2. Acids referred to in this part of ISO 5667 are commercially available “concentrated” acids.

All reagents shall be labelled with a “shelf-life”. The shelf-life represents the period for which the reagent is suitable for use, if stored correctly. This shelf-life shall not be exceeded. Any reagents that are not completely used by the expiry of the shelf-life date shall be discarded.

NOTE Often the shelf-life of reagents is supplied by the receiving laboratory.

Check reagents periodically, e.g. by field blanks, and discard any reagent found to be unsuitable.

Between on-site visits, reagents shall be stored separately from sample containers and other equipment in a clean, secure cabinet in order to prevent contamination.

Each sample shall be labelled accordingly, after the addition of the preservative. Otherwise, there could be no visible indication as to which samples have been preserved, and which have not.

5.1 Solids

5.1.1 Sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$, $w(Na_2S_2O_3 \cdot 5H_2O) > 99\ \%$.

5.1.2 Ascorbic acid, $C_6H_8O_6$, $w(C_6H_8O_6) > 99\ \%$.

5.1.3 Sodium hydroxide, NaOH, $w(NaOH) > 99\ \%$.

5.1.4 Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$, $w(Na_2B_4O_7 \cdot 10H_2O)$, > 99 %.

CAUTION Sodium tetraborate decahydrate is known to be a carcinogen, mutagen and reproductive toxin (CMR).

5.1.5 Hexamethylenetetramine (hexamine, urotropine), $C_6H_{12}N_4$, $w(C_6H_{12}N_4) > 99\ \%$.

5.1.6 Potassium iodide, KI, $w(KI) > 99\ \%$.

5.1.7 Iodine, I_2, $w(I_2) > 99\ \%$.

5.1.8 Sodium acetate, $C_2H_3NaO_2$, $w(C_2H_3NaO_2) > 99\ \%$.

5.1.9 Ethylenediamine, $C_2H_8N_2$, $w(C_2H_8N_2) > 99\ \%$.

5.2 Solutions

5.2.1 Zinc acetate solution $C_4H_6O_4Zn$ (10 g/l).

Dissolve 10,0 g of zinc acetate in ~100 ml of water . Dilute to 100 ml with water. Store the solution in a polypropylene or glass bottle for a maximum period of 1 a.

5.2.2 Orthophosphoric acid ($\rho \approx 1{,}7$ g/ml), H_3PO_4, $w(H_3PO_4) > 85\ \%$, $c(H_3PO_4) = 15$ mol/l.

5.2.3 Hydrochloric acid ($\rho \approx 1{,}2$ g/ml), HCl, $w(HCl) > 36\ \%$, $c(HCl) = 12{,}0$ mol/l.

5.2.4 Nitric acid ($\rho \approx 1{,}42$ g/ml), HNO_3, $w(HNO_3) > 65\ \%$, $c(HNO_3) = 15{,}8$ mol/l.

5.2.5 Sulfuric acid ($\rho \approx 1{,}84$ g/ml), H_2SO_4 (freshly prepared).

Dilute concentrated sulfuric acid (H_2SO_4), $\rho \approx 1{,}84$ g/ml, $w(H_2SO_4) \approx 98\ \%$ 1 + 1 by carefully adding the concentrated acid to an equal volume of water and mix.

WARNING — Adding the concentrated acid to the water can give violent reactions because of an exothermic reaction.

5.2.6 Sodium hydroxide solution ($\rho \approx 0{,}40$ g/ml), NaOH.

5.2.7 Formaldehyde solution (formalin), CH_2O, $\phi(CH_2O) = 37\ \%$ to 40 % (freshly prepared),

WARNING — Beware of formaldehyde vapours. Do not store large numbers of samples in small work areas.

5.2.8 Disodium salt of ethylenediaminetetraacetic acid (EDTA) ($\rho \approx$ 0,025 g/ml), $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, $w(C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O) > 99$ %.

Dissolve 25 g EDTA in 1 000 ml of water.

5.2.9 Ethanol C_2H_5OH, $\phi(C_2H_5OH) = 96$ %.

5.2.10 Alkaline Lugol's solution, 100 g potassium iodide (5.1.6), 50 g iodine (5.1.7), and 250 g sodium acetate (5.1.8) in 1 000 ml water to pH 10.

5.2.11 Acidic Lugol's solution, 100 g potassium iodide (5.1.6), 50 g iodine (5.1.7) and 100 ml glacial acetic acid (5.2.17) in 1 000 ml water to pH 2.

5.2.12 Neutralized formaldehyde solution, formaldehyde solution (5.2.7) neutralized with sodium tetraborate (5.1.4) or hexamethylenetetramine (5.1.5). Formalin solution at 100 g/l gives a final solution of $\phi(CH_2O) = 3{,}7$ % to 4,0 %.

WARNING — Beware of formaldehyde vapours. Do not store large numbers of samples in small work areas.

5.2.13 Ethanol preservative solution.

Ethanol (5.2.9), formaldehyde solution (5.2.7*)* and glycerol (5.2.18) (100 + 2 + 1 parts by volume, respectively).

5.2.14 Sodium hypochlorite NaOCl, $w(NaOCl) = 10$ %. Dissolve 100 g sodium hypochlorite (NaOCl) in 1 000 ml of water.

5.2.15 Potassium iodate KIO_3, $w(KIO_3) = 10$ %. Dissolve 100 g potassium iodate (KIO_3) in 1 000 ml of water.

5.2.16 Methanoic acid (formic acid) CH_2O_2, $\phi(CH_2O_2) > 98$ %.

5.2.17 Glacial acetic acid $C_2H_4O_2$, $w(C_2H_4O_2) > 99$ %.

5.2.18 Glycerol (glycerin, glycerine) $C_3H_5(OH)_3$.

5.3 Materials

5.3.1 Container and cap, types as specified in Tables A.1 to A.3.

5.3.2 Filter, pore size 0,40 µm to 0,45 µm, unless a different filter size is specified in the analytical International Standard.

6 Containers

6.1 Container selection and preparation

The choice of sample container (5.3.1) is of major importance and ISO 5667-1 provides some guidance on this subject.

Details of the type of container used for the collection and storage of samples are given in Tables A.1 to A.3. The same considerations given to this selection of suitable container material shall also be given to the selection of cap liner materials.

Sample containers shall be made of a material appropriate for preserving the natural properties of both the sample and the expected range of contaminants. Suitable types of containers for each analyte to be measured are given in Tables A.1 to A.3.

NOTE For very low concentrations of metals, containers prescribed can be different from those used for higher concentrations. Details can be found in Table A.1 or in the analytical International Standards.

If the samples are to be frozen, suitable containers, such as polyethylene (PE) or polytetrafluoroethylene (PTFE), shall be used to prevent breakage.

The use of disposables is preferred. Some manufacturers supply containers with a certificate of cleanliness. If such a certificate of cleanliness is supplied, it is not necessary to clean or rinse the containers before use.

6.2 Filtration on site

Filtration on site is required in some cases.

- Groundwaters shall be filtered on site if dissolved metals need to be analysed.
- Waters shall be filtered (5.3.2) on site, if this is required according to Annex A. Unless specified otherwise, a filter pore size 0,40 µm to 0,45 µm shall be used.

If immediate filtration on site is impossible, then the reason and the time between sampling and filtration shall be added to the test report.

6.3 Filling the container

The container (5.3.1) shall be filled completely unless prescribed differently in Tables A.1 to A.3 or the analytical International Standard used. If the samples are to be frozen as part of their preservation, sample containers shall not be completely filled. This is in order to prevent breakage which may arise from expansion of ice during the freezing and thawing process.

If no preservatives are present in the bottle, then prerinsing the bottle may be advisable. Guidance on prerinsing can be found in ISO 5667-14.

7 Sample handling and preservation

7.1 Sample handling and preservation for physical and chemical examination

Waters, particularly fresh waters, waste waters and groundwaters, are susceptible to changes as a result of physical, chemical or biological reactions which may take place between the time of sampling and the commencement of analysis. The nature and rate of these reactions are often such that, if precautions are not taken during sampling, transport and storage (for specific analytes), the concentrations determined are different to those existing at the time of sampling.

The extent of these changes is dependent on the chemical and biological nature of the sample, its temperature, its exposure to light, the type of the container in which it is placed, the time between sampling and analysis, and the conditions to which it is subjected, e.g. agitation during transport. Further specific causes of variation are listed in a) to f).

a) The presence of bacteria, algae and other organisms can consume certain constituents of the samples. These organisms can also modify the nature of the constituents to produce new constituents. This biological activity affects, for example, the concentrations of dissolved oxygen, carbon dioxide, compounds of nitrogen, phosphorus and, sometimes, silicon.

b) Certain compounds can be oxidized either by dissolved oxygen present in the samples, or by atmospheric oxygen [e.g. organic compounds, Fe(II) and sulfides].

c) Certain substances can precipitate out of solution, e.g. calcium carbonate, metals, and metallic compounds such as $Al(OH)_3$, or can be lost to the vapour phase (e.g. oxygen, cyanides, and mercury).

d) Absorption of carbon dioxide from air can modify pH, conductivity, and the concentration of dissolved carbon dioxide. Passage of compounds like ammonia and silicon fluoride through some types of plastics may also affect pH or conductivity.

e) Dissolved metals or metals in a colloidal state, as well as certain organic compounds, can be irreversibly adsorbed on to the surface of the containers or solid materials in the samples.

f) Polymerized products can depolymerize, and conversely, simple compounds can polymerize.

Changes to particular constituents vary both in degree and rate, not only as a function of the type of water, but also, for the same water type, as a function of seasonal conditions.

These changes are often sufficiently rapid to modify the sample considerably in a short time. In all cases, it is essential to take precautions to minimize these reactions and, in the case of many analytes, to analyse the sample with a minimum of delay. If the required precaution for changes is filtration on site, then a filter (5.3.2) shall be used.

Details of the sample preservation are given in Table A.1.

7.2 Sample handling and preservation for biological examination

The handling of samples for biological examination is different from that for samples requiring chemical analysis. The addition of chemicals to the sample for biological examination can be used for either fixation and/or preservation of the sample. The term “fixation” is defined as the protection of morphological structures, while the term “preservation” is defined as the protection of organic matter from biochemical or chemical degradation. Preservatives, by definition, are toxic, and the addition of preservatives may lead to the death of living organisms. Prior to death, irritation may cause the most delicate organisms, which do not have strong cell walls, to collapse before fixation is complete. To minimize this effect, it is important that the fixation agent enter the cell quickly.

IMPORTANT Acidic Lugol’s solutions (5.2.11) can lead to the loss of structures in organisms or also lead to the loss of small organisms (e.g. some flagellates); in this case, use an alkaline Lugol’s solution (5.2.10), e.g. during the summer, when the appearance of silico-flagellates is frequently observed.

The fixing and/or preservation of samples for biological examination shall meet the following criteria:

a) the effect of the fixative, and/or preservative, on the loss of the organism shall be known beforehand;

b) the fixative or preservative shall effectively prevent the biological degradation of organic matter at least during the storage period of the samples;

c) the fixative, and/or preservative, shall enable the biological analyte (e.g. organisms or taxonomical groups) to be assessed during the storage period of the samples.

Details of the preservation of samples are given in Table A.2.

7.3 Sample handling and preservation for radiochemical analysis

WARNING — Radioprotection such as shielding may be necessary, depending on the activity of the sample.

There is little difference between the handling of samples for radiochemical analysis and the handling of samples for physicochemical analysis.

The delay between sampling and measurement has to be consistent with the radioactive half-life of the radionuclides of interest. The conditions to be taken for adequate storage are independent of the radioactive half-life, but identical to those required for the corresponding stable isotope.

NOTE Cooling radiological samples is primarily used to prevent algal growth and biological spoilage. It is not a necessary preservation step for radiochemical analyses. These samples are often combined with those for physical, chemical or biological analysis.

8 Sample transport

Cooling or freezing procedures shall be applied to samples to increase the time period available for transport and storage and if required by Tables A.1 to A.3. When transport takes place, the sampling plan (e.g. ISO 5667-1) shall consider:

- the time between sampling and start of transport;
- transport time;
- starting time of analysis in the laboratory.

This sum of these three periods is limited to the maximum storage times according to Tables A.1 to A.3.

If the maximum storage time cannot be met, then the sampling plan shall be reformulated to allow these requirements to be accommodated.

A cooling temperature of the device during transport of (5 ± 3) °C has been found suitable for many applications. Cooling and freezing procedures applied shall be in line with instructions from the analytical laboratory. Freezing especially requires detailed control of the freezing and thawing process in order to return the sample to its initial equilibrium after thawing.

Containers holding samples shall be protected and sealed during transport in such a way that the samples do not deteriorate or lose any part of their content. Container packaging shall protect the containers from possible external contamination, particularly near the opening, and should not itself be a source of contamination.

Glass containers shall be protected from potential breakage during transport by appropriate packaging. Samples shall be transported as soon as possible after sampling and with cooling if necessary according to Tables A.1 to A.3.

Laboratory samples for dispatch or transport by third parties and preserved laboratory samples should be sealed in such manner that the integrity of the sample can be maintained.

Samples required for (potential) regulatory investigations should be sealed to a level that meets the requirements of the authorities or other organization(s) concerned with the transport of the sample.

During transportation samples shall be stored in a cooling device capable of maintaining a temperature of (5 ± 3) °C. For proper evaluation of the conditions during transport a device capable of recording the (maximum) temperature of the air surrounding the sample may be used.

NOTE Devices capable of logging of the air temperature during the transportation are available, but their use and adequate calibration can be costly.

9 Identification of samples

Container labels should withstand wetting, drying and freezing without detaching or becoming illegible. The labelling system shall be waterproof to allow use on site.

The exact information given in the sampling report and on the sample labels depends on the objectives of the particular measurement programme. In all cases, an indelible label shall be secured to the sample container.

For each sample, at least the following information shall be available.

A unique identifier, traceable to

- date, time and location of sampling;
- sample number;
- description of sample;
- name of sampling personnel;
- details of sample preservation, or fixation used;
- details of sample storage used;
- any information regarding integrity and manipulation of the sample;
- any other information, as necessary.

A unique identifier, traceable to sample date, location, and sample number shall appear on the label of the sample container.

All other information is supplementary and should be detailed in the sample report.

10 Sample reception

All information regarding sample, handling and storage shall be included in a sampling report.

Laboratory staff shall receive and check information on sample preservation and sample transport conditions.

In all cases, and especially when a “chain of custody” process needs to be established, the number of sample containers received in the laboratory shall be verified against the number of sample containers submitted.

11 Sample storage

The storage duration of the water samples within the laboratory is specific to the analyte(s) to be analysed. Samples shall be stored no longer than the maximum storage period given in Tables A.1 to A.3. The maximum storage time includes the time of transport to the laboratory (3.4).

The refrigeration conditions within the laboratory shall be (3 ± 2) °C. Where samples are frozen for preservation, unless otherwise specified, the temperature shall be maintained below −18 °C. Exceptions to these refrigeration conditions are listed in Tables A.1 to A.3.

When thawing frozen samples it is recommended that each sample container be placed in a separate secondary container to minimize the risk of liquid loss, should a split become apparent during the thawing process or a rupture occur during initial freezing and storage. A mild impact can cause splitting of some plastics at low temperatures.

With respect to thawing, it is recommended that this be done under ambient conditions, unless specified otherwise in Tables A.1 to A.3 or the analytical International Standard being used.

Annex A
(informative)

Techniques for sample preservation

A.1 General

This part of ISO 5667 and the analytical International Standards listed in this annex are complementary. See the Notice on page 1.

In some cases the alternative preservation techniques listed contradict each other. It is intended that where an existing analytical International Standard is used, the preservation technique described in that method applies. However, alternative preservation techniques given in this part of ISO 5667 can also be appropriate. Where no preservation method is described in the analytical International Standard, or no analytical International Standard is used, the technique(s) listed in this part of ISO 5667 shall be used.

A validation protocol used for validation studies can be found in Annex C. Reports and data regarding validation are listed in the bibliography.

A.2 Abbreviations for plastics

FEP	perfluoro(ethylene/propylene)	PFA	perfluoroalkoxy (polymer)
PE	polyethylene	PP	polypropylene
PE-HD	high density polyethylene	PTFE	polytetrafluoroethylene
PET	polyethylene terephthalate	PVC	poly(vinyl chloride)

A.3 Physicochemical and chemical analysis

See Table A.1. The following general remarks should be noted in relation to use of Table A.1.

- A preservation time of 1 d means that if 24 h is exceeded, this should be stated in the report.
- The types of containers are identical to those in the analytical International Standards. In some cases, the type of container in the standard is very specific, e.g. PTFE. This is essential when very low concentrations have to be measured. In other cases, when the specific type of plastic is not important, the term plastics is sufficient.

A.4 Biological analysis

The following general remarks should be noted in relation to use of Table A.2.

- Plastics used for containers in the laboratory are for instance PE, PTFE, PET, PP, PFA, and FEP.
- If a preservation period is not specified, it is generally unimportant. The indication “1 month” represents preservations without particular difficulty.

A.5 Radiochemical analytes and activities

The following general remarks should be noted in relation to use of Table A.3.

WARNING — Radioprotection such as shielding may be necessary, depending on the activity of the sample.

- Acidification is carried out to avoid algal growth, biological spoilage, and adsorption of metal ions to the inner wall of the sample container.
- Contamination of the sample should be avoided, especially if the sample activity is very low. Some sample sites can have measurable activity in the soil or air, or in waters other than those being sampled. Laboratories, as well as some items of domestic equipment, can contain radioactive material. When sampling precipitation, any special requirements in this table are additional to those given in ISO 5667-8. As the collection of sufficient sample can require a period of days, both the starting and finishing times and dates should be recorded. A record of precipitation collection for the sample station for the appropriate period should be appended. Stabilizer or carrier may be added, if appropriate for the analytes being measured.
- Plastics used for containers in the laboratory are for instance PE, PTFE, PET, PP, PFA, and FEP.

NOTE Some plastics bottles slowly concentrate samples over a period of many months by being very slightly permeable to water. Also see the comments for e.g. radon.

Table A.1 — Techniques for sample preservation — Physicochemical and chemical analysis

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Acidity and alkalinity		Plastics or glass	For samples high in dissolved gases, analyse preferably on site. Reduction and oxidation during storage can change the sample	14 d	Best practice
	ISO 9963-1:1994[18] No reference to this part of ISO 5667	PE, borosilicate glass	For samples high in dissolved gases, analyse preferably on site		
Adsorbable organic halides (AOX)	ISO 9562:2004[17] No reference to this part of ISO 5667	Plastics or glass Glass is required if the concentration is suspected to be low	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4).·Store samples in the dark or use dark-coloured bottles. If samples are chlorinated, note c applies	5 d	Best practice
		Plastics	Freeze to below –18 °C	1 month	Best practice
Aluminium	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 12020:1997[36] No reference to this part of ISO 5667	Suitable plastics, no polyolefins (may contain traces of Al)			
	ISO 10566:1994[27] Refers normatively to ISO 5667-3:1994	PE			

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Ammonium		Plastics or glass	Waters shall be filtered on site. Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5)	21 d	Best practice
	ISO 7150-1:1984[7] No reference to this part of ISO 5667	Plastics or glass	Waters shall be filtered on site	1 d	Validated[67]
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667	PE	Waters shall be filtered on site. Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)	14 d	Best practice
	ISO 11732:2005[33] Refers normatively to this part of ISO 5667	Glass, polyolefins, PTFE	Waters shall be filtered on site. Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5). Store samples in the dark or use dark-coloured bottles		
		Plastics	Waters shall be filtered on site Freeze to below −18 °C	1 month	Best practice
Anions: See the individual anions (Br⁻, F⁻, Cl⁻, NO_2^-, NO_3^-, SO_4^{2-} ,- and PO_4^-)					
Antimony	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HCl (5.2.3) or HNO_3 (5.2.4). HCl (5.2.3) should be used if the hydride technique is used for analysis	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Arsenic	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HCl (5.2.3) or HNO_3 (5.2.4). HCl (5.2.3) should be used if the hydride technique is used for analysis	6 months	Validated[88]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 11969:1996[35] Refers normatively to ISO 5667-3:1994	PE, borosilicate glass, prerinsed with nitric acid (10 % volume fraction)			

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Barium	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Beryllium	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			
Biochemical oxygen demand (BOD)		Plastics or glass	Store samples in the dark or use dark-coloured bottles	1 d	Best practice
		Plastics	Freeze to below −18 °C. Store samples in the dark or use dark-coloured bottles	1 month (6 months if >50 mg/l)	Validated[88]
Boron	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			
Bromate	ISO 15061:2001[42] Refers normatively to ISO 5667-3:1994	PE	Remove any ozone from the sample, for example, add 50 mg of ethylenediamine (5.1.9) to 1 l of sample immediately after sampling	1 month	Best practice
Bromide and bromine compounds	ISO 10304-1:2007[21] Refers normatively to this part of ISO 5667	PE or glass		1 month	Best practice
Bromine residual		Plastics or glass, dark coloured	Analyse on site	5 min	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Cadmium	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 5961:1994[3] Refers normatively to this part of ISO 5667	PE, borosilicate glass			
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP:			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Calcium	ISO 7980:1986[10] No reference to this part of ISO 5667	PE, PP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4) or HCl (5.2.3)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Carbon dioxide	ISO 9439[16] No reference to this part of ISO 5667	Plastics or glass	Analyse preferably on site.	1 d	Best practice
Carbon, total organic (TOC)	ISO 8245[13] Refers normatively to this part of ISO 5667	Plastics or glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5) or H_3PO_4.(5.2.2.) If loss of volatile organic compounds is suspected due to release of carbon dioxide upon acidification, then acidification is not suitable. Cool and analyse within 8 h. Freeze to below –18 °C	7 d	Best practice
		Plastics		1 month	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Carbon, dissolved organic (DOC)	ISO 8245[13] Refers normatively to this part of ISO 5667	Plastics or glass	Waters shall be filtered before acidifying to pH 1 to pH 2 with H_2SO_4 (5.2.5) or H_3PO_4. (5.2.2)	7 d	Best practice
			Freeze to below −18 °C	1 month	Best practice
Chemical oxygen demand (CODCr)	ISO 15705:2002[48] Refers normatively to ISO 5667-3:1994	Plastics or glass	Acidify to pH 1 to pH 2 with H_2SO_4.(5.2.5)	6 months	Validated[88]
		PP, glass			
		Plastics	Freeze to below −18 °C	6 months	Validated[88]
		Plastics			
Chloramine		Plastics or dark glass	Analyse on site	5 min	Best practice
Chlorate	ISO 10304-4:1997[23] Refers normatively to ISO 5667-3:1994	Plastics or glass	Add NaOH (5.1.3. or 5.2.6) to pH 10 ± 0,5	7 d	Best practice
Chloride	ISO 15682:2000[47] Refers to this part of ISO 5667 informatively	PE or glass	None required, common techniques do not have an adverse effect	1 month	Best practice
	ISO 10304-4:1997[23] Refers normatively to ISO 5667-3:1994	Plastics or glass			
Chlorinated solvents: See *Volatile organic compounds*					
Chlorine dioxide		Plastics or dark glass	None required, analyse on site	5 min	Best practice
Chlorine, residual		Plastics or dark glass	Analyse on site	5 min	Best practice
Chlorite	ISO 10304-4:1997[23] Refers normatively to ISO 5667-3:1994	Plastics or dark glass	Add NaOH (5.1.3 or 5.2.6) to pH 10 ± 0,5	7 d	Best practice
Chlorophyll	ISO 10260:1992[20] No reference to this part of ISO 5667	Plastics or glass	Filter (5.3.2) preferably on site. Store samples in the dark or use dark-coloured bottles	1 d	Best practice
			After filtration (5.3.2) and extraction with hot ethanol, freeze to below −18 °C	extract 1 month	
			After filtration (5.3.2), freeze to below −18 °C	filter plus residue 14 d	
			After filtration (5.3.2), freeze to below −80 °C	filter plus residue 1 month	

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Chromium	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Chromium(VI)	ISO 23913:2006[60] Refers normatively to this part of ISO 5667	Plastics or borosilicate glass		24 h	Best practice
	ISO 18412:2005[55] Refers normatively to this part of ISO 5667	Plastics or borosilicate glass		4 d	Best practice
Cobalt	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Colour	ISO 7887:2011[8] Refers normatively to this part of ISO 5667	Plastics or glass	Store samples in the dark or use dark-coloured bottles	5 d	Best practice
			For groundwater rich in iron(II), analyse on site	5 min	Best practice
Conductivity	ISO 7888:1985[9] Refers normatively to this part of ISO 5667	Plastics or glass except soda glass	Analyse preferably on site	1 d	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Copper	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Cyanide easily liberated		Plastics or glass	Add NaOH (5.1.3 or 5.2.6) to pH > 12. Store samples in the dark or use dark-coloured bottles	7 d 1 d if sulfide is present	Best practice
	ISO 14403:2012[40] Makes normative reference to this part of ISO 5667			3 d	Best practice
Cyanide, total		Plastics or glass	Add NaOH (5.1.3 or 5.2.6.) to pH > 12. Store samples in the dark or use dark-coloured bottles	14 d 1 d if sulfide is present	Validated[73]
	ISO 14403:2012[40] Makes normative reference to this part of ISO 5667			3 d	Best practice
Cyanochloride		Plastics		1 d	Best practice
Detergents: See *Surfactants*					
Dissolved solids (dry residue): See *Total solids (total residues)*					
Extractable organic halides (EOX) in surface and waste water		Glass	If samples are chlorinated, note c applies	4 d	Validated[84]
Extractable organic halides (EOX) in groundwater and drinking water		Glass	If samples are chlorinated, note c applies	1 month	Validated[84]
Extractable organic halides (EOX)		Glass	If samples are chlorinated, note c applies. Acidify to pH 1 to pH 2 with HNO_3 (5.2.4) or H_2SO_4 (5.2.5)	14 d	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Fluorides	ISO 10304-1:2007[21] Refers normatively to this part of ISO 5667	Plastics but not PTFE		1 month	Best practice
	ISO 10359-1:1992[24] Refers normatively to this part of ISO 5667				
	ISO 10359-2:1994[25] Refers normatively to ISO 5667-3:1994				
Hydrazine		Glass	Acidify with HCl (5.2.3) to 1 mol/l. Store samples in the dark or use dark-coloured bottles	1 d	Best practice
Hydrocarbons		Glass	Acidify to pH 1 to pH 2 with HCl (5.2.3), HNO_3 (5.2.4) or H_2SO_4 (5.2.5)	1 month	Best practice
	ISO 9377-2:2000[15] Refers normatively to ISO 5667-3:1994	Glass with ground glass stopper, or with screw cap, lined with PTFE		4 d	Best practice
Hydrogencarbonates: See *Acidity and alkalinity*					
Iodide	ISO 10304-3:1997[22] Refers normatively to ISO 5667-3:1994	PE or glass		1 month	Best practice
Iodine		Glass	Store samples in the dark or use dark-coloured bottles	1 d	Best practice
Iron(II)		Plastics or borosilicate glass	Acidify to pH 1 to pH 2 with HCl (5.2.3)	7 d	Best practice
Iron	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Kjeldahl nitrogen		Plastics or glass or borosilicate glass	Freeze to below –18 °C	6 months	Validated[88]
	ISO 5663:1984[1] No reference to this part of ISO 5667	Plastics or glass or borosilicate glass	Acidify to pH 1 to pH 2 with H_2SO_4.(5.2.5)	1 month	Best practice
Lead	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Lithium	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 14911:1998[41] Refers normatively to ISO 5667-3:1994	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Magnesium	ISO 7980:1986[10] No reference to this part of ISO 5667	PE, PP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 14911:1998[41] Refers normatively to ISO 5667-3:1994	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Manganese	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Mercury		Plastics or borosilicate glass	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Best practice
	ISO 17852:2006[53] Refers normatively to this part of ISO 5667	PTFE, FEP, borosilicate glass, quartz			
	ISO 12846:2012[37] Refers normatively to this part of ISO 5667	Plastics or borosilicate glass	Add HCl (5.2.3) 1 ml/100 ml Particular care is needed to ensure that the sample is free from contamination	2 d	Validated[37]
			Stabilization with digestion step using a potassium bromide–potassium bromate reagent takes place within the laboratory	1 month	Best practice
Molybdenum	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
Monocyclic aromatic hydrocarbons: See *Volatile organic compounds*					
Nickel	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[88]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Nitrate — all waters		Plastics or glass		1 d	Best practice
	ISO 13395:1996[38] Refers normatively to ISO 5667-3:1994	PE or glass		1 d	Best practice
		PE or glass	Freeze to below –18 °C	8 d	Best practice
		Plastics or glass	Acidify to pH 1 to pH 2 with HCl (5.2.3)	7 d	Best practice
		Plastics	Freeze to below –18 °C	1 month	Best practice
Nitrate in waste water and surface water		Plastics or glass	Waters shall be filtered on site	4 d	Validated[82][89]
Nitrite — all waters	ISO 13395:1996[38] Refers normatively to ISO 5667-3:1994	Plastics or glass	Analysis should preferably be carried out on site	1 d	Best practice
Nitrite in waste water and surface water		Plastics or glass	Waters shall be filtered on site	4 d	Validated[82][89]
Nitrogen total	ISO 29441:2010[62] Refers normatively to this part of ISO 5667	Plastics or glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5)[b]	1 month	Best practice
		Plastics	Freeze to below –18 °C	1 month	Best practice
Odour		Glass	A qualitative analysis can be carried out on site	6 h	Best practice
Oil and grease		Glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5) or HCl (5.2.3) or HNO_3 (5.2.4). Fill bottle to ~90 %, leave sufficient headspace	1 month	Best practice
Organic chlorine		Glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5) or HCl or HNO_3 (5.2.4)	1 month	Best practice
Organotin compounds	ISO 17353:2004[52] Refers normatively to this part of ISO 5667	Glass	Store samples in the dark or use dark-coloured bottles	1 d	Best practice
		Glass		7 d	Best practice
Orthophosphates, dissolved: See *Phosphorus, dissolved*					
Oxygen		Plastics or glass	Fix the oxygen on site. Store samples in the dark or use dark-coloured bottles	4 d	Best practice
		Plastics or glass	The electrochemical method may be used as well and can be carried out on site. Store samples in the dark or use dark-coloured bottles	1 d	Best practice
	ISO 5814:2012[2]	Plastics or glass	None required, analyse on site		

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Permanganate index (CODMn)	ISO 8467:1993[14] No reference to this part of ISO 5667	Plastics or glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5)	2 d	Best practice
		Plastics or glass	Store samples in the dark.	2 d	Best practice
		Plastics	Freeze to below –18 °C	1 month	Best practice
Pesticides, carbamates		Glass	If samples are chlorinated, note c applies	14 d	Best practice
		Plastics	Freeze to below –18 °C	1 month	Best practice
Pesticides, phenoxyalkanoic herbicides[a] **alkylhalogenated phenoxy acids, hydroxybenzonitriles and bentazone**		Glass with PTFE cap liner or septum	Acidify to pH 1 to pH 2 with HCl (5.2.3), HNO_3 (5.2.4) or H_2SO_4 (5.2.5)[c]	14 d	Best practice
			Acidify to between pH 3 to 4 with methanoic acid (5.2.16)[c]		
	ISO 15913:2000[49] Refers normatively to ISO 5667-3:1994	Glass, dark coloured		3 d	
Pesticides containing organochlorine and chlorobenzenes **α-endosulfan, β-endosulfan, endosulfan sulfate, *cis*-chlordane, *trans*-chlordane, *cis*-heptachlorepoxide, *trans*-heptachlorepoxide, heptachlor, α-HCH, β-HCH, γ-HCH, δ-HCH, aldrin, dieldrin, endrin, isodrin, telodrin, hexachlorobutadiene, *o,p*'-DDD, *o,p*'-DDE, *o,p*'-DDT, *p,p*'-DDD, *p,p*'-DDE, *p,p*'-DDT, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3,5, tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene**	ISO 6468:1996[4] No reference to this part of ISO 5667	Dark glass with PTFE cap liner	Sample endosulfan separately keep at pH < 2 others adjust to pH 5,0 to pH 7,5. If pH is outside that range, extract within 24 h	1 d	Best practice
		Dark glass with PTFE cap liner		7 d	Validated[68][69][71][75][77][80][82][83]
Pesticides containing organophosphorus	ISO 10695:2000[28] No reference to this part of ISO 5667	Dark glass with PTFE cap liner	Some organophosphorus compounds can degrade rapidly in an aqueous environment. Therefore, unless stability trials indicate otherwise, extract the sample within 1 d of collection of phosphorus compounds	1 d	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Pesticides containing organophosphorus **chlorpyrifos-ethyl, chlorpyrifos-methyl, diazinon, dichlorvos, dimethoate, disulfoton, fenthion, malathion mevinphos, parathion-ethyl, parathion-methyl**		Dark glass with PTFE cap liner		7 d	Validated[79][82]
Pesticides containing organophosphorus **glyphosate**	ISO 21458:2008[59] No reference to this part of ISO 5667	Plastics, e.g. polyolefin		6 d	Best practice
			Freeze to < −18 °C	1 month	Best practice
Pesticides containing organonitrogen	ISO 10695:2000[28] No reference to this part of ISO 5667	Dark glass with PTFE cap liner	Some organic nitrogen compounds can degrade rapidly in an aqueous environment. Therefore unless stability trials indicate otherwise, extract the sample within 2 d of collection for nitrogen compounds	2 d	Best practice
Pesticides containing organonitrogen	ISO 11369:1997[30] Refers normatively to ISO 5667-3:1994	Dark glass with PTFE cap liner		7 d	Best practice
Pesticides containing organonitrogen **atrazine, propazine, simazine, terbutryn**		Dark glass with PTFE cap liner		1 month	Validated[79][82]
Petroleum and derivatives: See *Hydrocarbons*					
pH	ISO 10523:2008[26] Refers normatively to this part of ISO 5667	Plastics or glass	Analyse preferably on site	1 d	Validated[66][85]
pH — (anaerobic) groundwater	ISO 10523:2008[26] Refers normatively to this part of ISO 5667	PE or glass. Exclude air by use of a specially shaped stopper			
Phenol index		Glass	Acidify to pH < 4 with H_3PO_4 (5.2.2) or H_2SO_4 (5.2.5)	21 d	Best practice
	ISO 14402:1999[39] Refers normatively to ISO 5667–3:1994	PTFE, glass	Acidify to pH < 4 with H_3PO_4.(5.2.2) or H_2SO_4 (5.2.5). Store samples in the dark or use dark-coloured bottles	21 d	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Phenols	ISO 8165-1:1992[11] Refers normatively to ISO 5667-3:1985	Glass or borosilicate glass with PTFE cap liner	Acidify to pH < 4 with H_3PO_4 (5.2.2) or H_2SO_4 (5.2.5)[c]	21 d	Best practice
	ISO 8165-2:1999[12] Refers normatively to ISO 5667-3:1994	Glass, dark coloured	pH < 2	7 d	Best practice
Phenols, alkylated	ISO 18857-1:2005[57] Refers normatively to this part of ISO 5667	Glass	Acidify to pH 2 with HCl (5.2.3) or H_2SO_4 (5.2.5)	14 d	Best practice
	ISO 18857-2:2009[58] Refers normatively to this part of ISO 5667	Glass with ground glass stopper, or with screw cap, lined with PTFE.			
Phenols, chlorinated	ISO 8165-1:1992[11] Refers normatively to ISO 5667-3:1985	Glass or borosilicate glass, with PTFE cap liner	If samples are chlorinated, note c applies	2 d	Best practice
	ISO 8165-2:1999[12] Refers normatively to ISO 5667-3:1994				
Phosphorus, dissolved		Plastics or glass or borosilicate glass	Waters shall be filtered on site. Before analysis, oxidizing agents may be removed by addition of iron(II) sulfate or sodium arsenite	1 month	Best practice
		Plastics	Freeze to below −18 °C		
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)		
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			
	ISO 6878:2004[5] No reference to this part of ISO 5667	Preferably glass, otherwise PE, PVC			

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Phosphorus, total		Plastics, glass or borosilicate glass	Acidify to pH 1 to pH 2 with H_2SO_4 (5.2.5) or HNO_3 (5.2.4)	1 month	Best practice
	ISO 15681-1:2003[45] Refers normatively to this part of ISO 5667	Plastics, glass or borosilicate glass			
	ISO 15681-2:2003[46] Refers normatively to this part of ISO 5667				
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			
	ISO 6878:2004[5] No reference to this part of ISO 5667	Preferably glass, otherwise PE, PVC			
		Plastics	Freeze to below −18 °C	6 months	Validated[88]
Phthalates	ISO 18856:2004[56] Refers normatively to this part of ISO 5667	Glass	Store samples in the dark or use dark-coloured bottles	4 d	Best practice
Polychlorinated biphenyls (PCBs)	ISO 6468:1996[4] No reference to this part of ISO 5667	Glass, with PTFE cap liner	Adjust to pH 5,0 to pH 7,5. If pH is outside that range, extract within 24 h	1 d	Best practice
			If samples are chlorinated, note c applies	7 d	Validated[68][69][71][75][77][80][82] [83]
Polycyclic aromatic hydrocarbons (PAHs)	ISO 17993:2002[54] Refers normatively to this part of ISO 5667	Glass, with PTFE cap liner	If samples are chlorinated, note c applies	7 d	Best practice
	ISO 28540:2011[61] Refers normatively to this part of ISO 5667			For naphthalene only 4 d	Validated[90]

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Potassium	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 9964-3:1993[19] No reference to this part of ISO 5667	PE			
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667		Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Selenium	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4). HCl (5.2.3) should be used if the hydride technique is used for analysis	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Silicates, dissolved		Plastics	Waters shall be filtered on site	1 month	Best practice
	ISO 16264:2002[50] No reference to this part of ISO 5667	Plastics	Waters shall be filtered on site. Analyse as soon as possible.	5 min	Best practice
Silicates, total		Plastics		1 month	Best practice
Silver	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667 ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Sodium	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
	ISO 9964-3:1993[19] No reference to this part of ISO 5667	PE			
	ISO 14911:1998[41] Refers normatively to this part of ISO 5667	PE	Acidify to pH 3 ± 0,5 with HNO_3 (5.2.4)		
Solids, suspended		Plastics or glass		2 d	Best practice
Sulfate	ISO 10304-1:2007[21] Refers normatively to this part of ISO 5667	Plastics or glass		1 month	Best practice
Sulfide (easily liberated)		Plastics	Fix the sulfide on site by adding 2 ml zinc acetate solution (5.2.1). Add NaOH (5.1.3) if the pH is not between 8,5 and 9,0	7 d	Best practice
			If samples are chlorinated, note c applies		
Sulfite	ISO 10304-3:1997[22] Refers normatively to ISO 5667-3:1994	Plastics or glass	Fix the sulfite on site by addition of 1 ml EDTA solution (5.2.8) per 100 ml of sample	2 d	Best practice
Surfactants, anionic		Glass		3 d	Best practice
			Add formaldehyde solution (5.2.12, see warning)	4 d	Best practice
			Freeze to below −18 °C	1 month	Best practice
Surfactants, cationic		Glass		2 d	Best practice
Surfactants, non-ionic		Glass	Add formaldehyde solution (5.2.12, see warning)	1 month	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Tin	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP	Acidify to pH 1 to pH 2 with HCl (5.2.3) or HNO_3 (5.2.4). HCl (5.2.3) should be used if the hydride technique is used for analysis	1 month	Validated[72]
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Total hardness: See *Calcium*					
Total solids (total residues, dry extract)		Plastics or glass		7 d	Best practice
Trihalomethanes: See *Volatile organic compounds*					
Turbidity	ISO 7027:1999[6] Refers normatively to ISO 5667-3:1994	Glass or plastics	Store samples in the dark or use dark-coloured bottles. Analyse preferably on site	1 d	Best practice
Uranium		Plastics or borosilicate glass	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
Vanadium	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	1 month	Best practice
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE For low concentrations: PFA, FEP			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667				
Volatile organic compounds **volatile halogenated hydrocarbons, monocyclic aromatic hydrocarbons and other solvent like organic compounds**		Glass, with PTFE cap liner or (head-space) vials with PTFE cap liner	Acidify to pH 1 to pH 2 with HCl (5.2.3), HNO_3 (5.2.4) or H_2SO_4 (5.2.5).[c] If samples are chlorinated, note c applies. For purge- and-trap, HCl (5.2.3) interferes	7 d	Validated[70][79][83]
	ISO 15680:2003[44] Refers normatively to this part of ISO 5667			5 d	Best practice
	ISO 11423-1:1997[31] No reference to this part of ISO 5667			2 d	Best practice
	ISO 11423-2:1997[32] No reference to this part of ISO 5667			2 d	Best practice
				1 d	Best practice

Table A.1 *(continued)*

Analyte to be studied	Reference International Standard	Type of container	Preservation and storage conditions additional to Clauses 8 and 11	Maximum storage times	Validated or Best practice
Zinc	ISO 15586:2003[43] Refers normatively to this part of ISO 5667	PE, PP, FEP	Acidify to pH 1 to pH 2 with HNO_3 (5.2.4)	6 months	Validated[85]
	ISO 11885:2007[34] Refers normatively to this part of ISO 5667	For normal concentrations: PE-HD, PTFE			
	ISO 17294-2:2003[51] Refers normatively to this part of ISO 5667	For low concentrations: PFA, FEP			

[a] According to ISO 15913:2000.[49]

[b] Not recommended for simultaneous persulfate oxidation/digestion procedures.

[c] If the sample is suspected to have been chlorinated, for each 1 000 ml of sample, add 80 mg of $Na_2S_2O_3.5H_2O$ (5.1.1) to the container after collection of sample (or after sampling).

Table A.2 — Techniques for the preservation of samples — Biological analysis

Organism group to be studied	Type of container	Preservation technique within the laboratory	Maximum recommended preservation time before analysis	Comments
Counting and identification				
Benthic macro-invertebrates, large samples	Plastics or glass	Add ethanol (5.2.9) to the sample to give a final volume fraction of 70 % to 75 %	1 year	Water in samples should first be decanted, rinsed in deionized water, and returned for storage in the ethanol solution
Benthic macro-invertebrates, small samples (e.g. reference collections)	Glass	Transfer to ethanol preservative solution (5.2.13 – see warning to 5.2.12)	Indefinitely	Special methods are required for invertebrate groups that are distorted by normal preservative treatment (e.g. platyhelminthes)
Algae and phytoplankton	Glass or plastics with tight fitting lid	Addition of 0,5 part to 1 part by volume of [acid (5.2.10) or alkaline (5.2.11)] Lugol's solution to 200 parts by volume of sample. Cool to (3 ± 2) °C	6 months	Store samples in the dark. Alkaline Lugol's solution (5.2.11) is generally applicable in fresh water and acidic Lugol's solution (5.2.10) in marine water with delicate flagellates. For specific determination, see specific standard. Addition of more Lugol's solution may be necessary if decolourization occurs. Oversaturation (deep/brown colouring) should be avoided, yet enough Lugol's solution(5.2.10 or 5.2.11) should be added to turn the sample to a cognac or straw colour. Fill bottle to ~90 %, leave sufficient headspace to allow homogenization
Microalgae	Glass or plastics with tight fitting lid	Addition of 0,5 part to 1 part by volume of [acid (5.2.10) or alkaline (5.2.11)] Lugol's solution to 200 parts by volume of sample. Cool to (3 ± 2) °C	6 months	Store samples in the dark. Alkaline Lugol's solution(5.2.11) is generally applicable in fresh water and acidic Lugol's solution(5.2.10) in marine water with delicate flagellates. For specific determination see specific standard. Addition of more Lugol's solution may be necessary if decolourization occurs. Over saturation (deep/brown colouring) should be avoided, yet enough Lugol's solution(5.2.10 or 5.2.11) should be added to turn the sample to a cognac or straw colour. Fill bottle to ~90 %, leave sufficient headspace to allow homogenization
		Freeze to below −18 °C	1 year	Special procedures may be necessary with groups which are changed by standard applied preservation methods

Table A.2 *(continued)*

Organism group to be studied	Type of container	Preservation technique within the laboratory	Maximum recommended preservation time before analysis	Comments
Macrophytes	Glass or plastics with tight fitting lid	Add ethanol (5.2.9) to the sample to give a final volume fraction of 70 % to 75 %	6 months	Fill bottle to ~90 %, Leave sufficient headspace to allow homogenization
		Freeze to below −18 °C	1 year	Special procedures may be necessary with groups which are changed by standard applied preservation methods
Benthic diatoms	Glass or plastics with tight fitting lid	Addition of 0,5 part to 1 part by volume of [acid (5.2.10) or alkaline (5.2.11)] Lugol's solution to 200 parts by volume of sample. Cool to (3 ± 2) °C	6 months	Store samples in the dark. Alkaline Lugol's solution(5.2.11) is generally applicable in fresh water and acidic Lugol's solution(5.2.10) in marine water with delicate flagellates. For specific determination see specific standard. Addition of more Lugol's solution may be necessary if decolourization occurs. Over saturation (deep/brown colouring) should be avoided, yet enough Lugol's solution(5.2.10 or 5.2.11) should be added to turn the sample to a cognac or straw colour. Fill bottle to ~90 %, Leave sufficient headspace to allow homogenization
		Add ethanol (5.2.9) to the sample to give a final volume fraction of 70 % to 75 %	6 months	Fill bottle to ~90 %, Leave sufficient headspace to allow homogenization
Pelagic diatoms	Glass or plastics with tight fitting lid	Addition of 0,5 part to 1 part by volume of [acid (5.2.10) or alkaline (5.2.11)] Lugol's solution to 200 parts by volume of sample. Cool to (3 ± 2) °C	6 months	Store samples in the dark. Alkaline Lugol's solution(5.2.11) is generally applicable in fresh water and acidic Lugol's solution(5.2.10) in marine water with delicate flagellates. For specific determination see specific standard. Addition of more Lugol's solution may be necessary if decolourization occurs. Over saturation (deep/brown colouring) should be avoided, yet enough Lugol's solution(5.2.10 or 5.2.11) should be added to turn the sample to a cognac or straw colour. Fill bottle to ~90 %, Leave sufficient headspace to allow homogenization
Zooplankton	Plastics or glass	Add ethanol (5.2.9) to the sample to give a final volume fraction of 70 % to 75 %	1 year	Suitable for crusteaceans and rotiferans.
		Add neutralized formaldehyde solution (5.2.12, see warning)	1 year	
		Add acidic Lugol's solution (5.2.11)	6 months	Addition of more acidic Lugol's solution (5.2.11) may be necessary if decolourization occurs.
Fresh and dry mass				

Table A.2 *(continued)*

Organism group to be studied	Type of container	Preservation technique within the laboratory	Maximum recommended preservation time before analysis	Comments
Benthic macro-invertebrates, macrophytes, algae, zooplankton, fish	Plastics or glass	Cool to (3 ± 2) °C	24 h	Do not freeze to below −18°C. The analysis should be carried out as soon as possible and not later than 24 h
	Plastics or glass	Add neutralized formaldehyde solution (5.2.12, see warning)	3 months minimum preservation time before analysis	Note that fresh and dry (bio)mass determinations of periphyton and phytoplankton are usually based on the cell volume measurements made during counting and identification procedure from the preserved sample
Mass of ash				
Benthic macro-invertebrates, macrophytes, algae,	Plastics or glass	Add neutralized formaldehyde solution (5.2.12, see warning)	3 months minimum preservation time before analysis	Note that fresh and dry (bio)mass determinations of periphyton and phytoplankton are usually based on the cell volume measurements made during counting and identification procedure from the preserved sample
Dry mass and mass of ash				
Zooplankton	Plastics or glass	Freeze to below −18 °C	6 months	Sample is filtered through preweighed glass-fibre membrane filters and then frozen to below −18 °C

Table A.3 — Techniques for sample preservation — Radiochemical analytes and activities

Analyte or activity to be studied	Type of container	Preservation technique	Maximum recommended preservation time before analysis	Comments
Gross alpha-activity	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4)	1 month	Do not acidify if the sample is evaporated immediately on a planchette for analysis. Without acidification, however, store samples in the dark and cool to (3 ± 2) °C if possible
		None	7 d	
Gross beta-activity (except iodine radioisotopes)	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4)	1 month	Do not acidify if the sample is evaporated immediately on a planchette for analysis. Without acidification, however, store samples in the dark and cool to (3 ± 2) °C if possible
		None	7 d	
Gamma-emitters	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4)	1 month	If possible, store samples in the dark and cool to (3 ± 2) °C. If a sample is not acidified, storage may be shorter if metal present are easily hydrolysed
		None	7 d	
Actinides **(alpha-emitters such as uranium, plutonium, americium, curium)**	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4)	2 months	If possible, store samples in the dark and cool to (3 ± 2) °C
		None	7 d	
^{14}C	Plastics	Add NaOH (5.2.4) to pH > 10	1 month	Fill bottle completely, leave no headspace and do not stir If possible, store samples in the dark and cool to (3 ± 2) °C
		None	5 d	Only if pH > 7, fill the container completely to avoid any exchange between sample and the air above. If possible, store samples in the dark and cool to (3 ± 2) °C
Iodine (radioisotopes)	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4). Where iodine-isotopes are measured with gross-beta-detection techniques, add KIO_3 (5.2.15) to prevent losses during evaporation	7 d	For gamma-spectrometry, acidification is sufficient. For gross beta-determination, acidify to pH < 1 with HNO_3 (5.2.4); add 2 ml to 4 ml of NaOCl (5.1.2.14) per litre of sample, ensuring an excess of free chlorine. If possible, store samples in the dark and cool to (3 ± 2) °C
Radon isotopes	Glass	Cool to (3 ± 2) °C	1 d	Fill bottle completely, leave no headspace and do not stir. If possible, store samples in the dark

Table A.3 *(continued)*

Analyte or activity to be studied	Type of container	Preservation technique	Maximum recommended preservation time before analysis	Comments
Radium	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4).	2 months	If possible, store samples in the dark and cool to (3 ± 2) °C
		None	2 months	
Strontium radioisotopes	Plastics	Acidify to pH < 2 with HNO_3 (5.2.4)	2 months	If possible, store samples in the dark and cool to (3 ± 2) °C
Tritium	Plastics, glass		3 months	Fill bottle completely, leave no headspace and do not stir. If samples are analysed without distillation, store samples in the dark and cool to (3 ± 2) °C if possible

Annex B
(informative)

Container preparation

B.1 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade and distilled or demineralized water or water of equivalent purity.

B.1.1 Acetone (IUPAC: propanone).

B.1.2 Hydrochloric acid, 4 % volume fraction and 25 % volume fraction HCl.

B.1.3 Nitric acid, 10 % volume fraction HNO_3.

B.2 Solvent-washed glass containers

WARNING — Organic solvents can be hazardous. Provide suitable handling facilities and handle with care.

Non-disposable sample containers and lids for semi-volatile analysis should be washed with a phosphate-free detergent solution, followed by thorough rinses with hot tap-water and analyte-free water. The last step should be an acetone rinse. The lids should be in place on the container during the rinse step (solvent in the container with the lid tightly screwed down) because the solvents can rinse plastic from the interior screw threads on to the PTFE lining.

For analysis of volatile organic compounds, sample containers, screw caps, and septa (silicone vapour barriers) should be washed with a phosphate-free detergent, rinsed once with tap-water, rinsed at least twice with analyte-free water, then dried at greater than 105 °C. A solvent rinse should generally be avoided because it can interfere with the analysis, although a methanol rinse is acceptable.

Alternatively, single use disposable containers and lids may be used for both sample types.

B.3 Acid-washed containers

For trace metal analysis, new sample containers should always be used. Sample containers and lids should be thoroughly cleaned with a phosphate-free detergent solution, thoroughly rinsed with metal-free water, soaked for 24 h in ~10 % volume fraction HNO_3 or ~25 % volume fraction HCl, and rinsed with metal-free water.

B.4 Containers for biological samples

Containers for the collection of toxicological or hydrobiological samples should be washed with a phosphate-free detergent solution, triple rinsed with hot tap-water and should be finished with a 4 % volume fraction hydrochloric acid rinse. It is possible to use disposable commercial plastic containers, subject to verification of the absence of interference with the analysis. Manipulation of the samples is often necessary, and the optimal methods depend on the study objectives.

Annex C
(informative)

Protocol as used in Dutch validation studies

C.1 General

Studies of the preservation of water samples were carried out in the Netherlands between 2003 and 2011. The studies were performed by laboratories associated with the Federation of Dutch laboratories, calibration and inspection bodies (FeNeLab). The objective was to establish preservation times for a number of critical analyses in the most relevant types of water: groundwater, surface water, and waste water.

A fixed protocol was used, which distinguished between four types of water: groundwater or eluate; surface water or effluent; food industry waste water; chemical industry waste water.

C.2 Protocol

Within each study, a minimum of between 6 and 12 different samples were used, at low and high concentration levels. Samples were obtained and divided over various bottles on day 0 and if necessary spiked. Day 0 is defined as the sampling date and date of arrival in the laboratory.

On day 0, analyses of eight test portions (bottles) were performed and the mean, $\overline{x}_\mathrm{A}$, of each analyte was calculated.

Subsequent measurements of three test portions were carried out each day in sequence, e.g. at 1 d, 2 d, 4 d, 7 d, 14 d, and 28 d. From the analytical results obtained, the mean of each analyte, $\overline{x}_\mathrm{B}$, was calculated.

Once the difference between the mean test results of the stored test portions and the mean test results on day 0 was more than twice the standard deviation, *s*, established by method validation, i.e.

$$\overline{x}_\mathrm{B} - \overline{x}_\mathrm{A} > 2s$$

the preservation time was considered to have been exceeded.

C.3 Studies performed

The studies concerned the following analyses and matrices:

- EOX in groundwater, surface water and waste water;
- nitrite and nitrate in surface water and waste water;
- pesticides containing organophosphorus or organonitrogen, in effluent and waste water;
- pesticides containing organochlorine and chlorobenzenes, in groundwater, surface water and waste water;
- polychlorinated biphenyls, in groundwater, surface water and waste water;
- volatile organic compounds (volatile halogenated hydrocarbons and aromatic hydrocarbons) in groundwater.

Additionally data provided by individual members of FeNeLab were evaluated. These data were obtained in stability studies for interlaboratory comparisons or for validation of procedures of sampling, transport and analysis of a specific laboratory.

C.4 Evaluations

The following analyses and matrices were evaluated:

- pH in drinking water, groundwater and surface water;
- pH in waste water;
- pesticides containing organochlorine and chlorobenzenes in surface water, groundwater and wastewater;
- polychlorinated biphenyls, in surface water, groundwater and wastewater;
- volatile organic compounds (volatile halogenated hydrocarbons and aromatic hydrocarbons) in waste water.

All reports and data involved are listed in the bibliography (References [66]–[86]) and are available at www.sikb.nl.

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[18] <std>ISO 9963-1:1994, *Water quality — Determination of alkalinity — Part 1: Determination of total and composite alkalinity*</std>

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[21] <std>ISO 10304-1:2007, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*</std>

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[23] <std>ISO 10304-4:1997, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 4: Determination of chlorate, chloride and chlorite in water with low contamination*</std>

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[26] <std>ISO 10523:2008, *Water quality — Determination of pH*</std>

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[28] <std>ISO 10695:2000, *Water quality — Determination of selected organic nitrogen and phosphorus compounds — Gas chromatographic methods*</std>

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