being chosen so that they adequately represent quality during the period of interest. The number required may be so large that it is impracticable to analyze them all. This problem can be, and often is, overcome by the use of composite samples, that is, one complete sample is formed by mixing portions of the individual samples in appropriate proportions (6, 23, 98). It is then necessary to analyze only one sample which indicates the average quality during the sampling period. Composite samples can also be formed by continuous or intermittent collection of samples in one container over a given period. This system has the advantage that the need for a separate compositing operation is avoided, and it may also facilitate the use of a greater sampling frequency. On the other hand, if analysis of the composite sample reveals some undesirable feature, it is not possible to determine at what time this feature developed. This would be possible if individual samples had been collected during the period.

Composite samples may also be used when it is required to obtain the average quality of a non-homogeneous water body. Individual samples are collected at appropriate positions, and then mixed in proportions governed by the volumes of the corresponding portions of the main water body. Such compositing is subject to essentially the same principles as compositing with respect to time, and is not further discussed here.

This procedure can, of course, be used only when it is the average that is of interest; a composite sample is incapable of giving any information on variations of quality during the sampling period. Nevertheless, compositing is often of value, and is often used in the analysis of rivers and effluents. For example, composites of 24 hourly-samples are used in measuring the qualities of effluents (99).

The proportions in which the individual samples are mixed are governed by the information required. If the average concentration is required, the volume taken of a sample should be directly proportional to the proportion of the total sampling period represented by that sample. Thus, if each sample were collected over an equal time period, equal volumes of each sample are taken. It is often necessary to estimate the average mass flow of a determinand; in this instance, the volumes taken of individual samples should be proportional to the corresponding flows at the times of sampling.

Certain precautions must be observed if composite samples are to give valid information:

i. The concentrations of determinands in individual samples must not change appreciably between collection and compositing; concentrations in the composite sample must not change appreciably before analysis (see Section 4.9.2). These requirements appear sometimes to be ignored.

ii. Compositing should not generally be used when the concentrations of determinands may be changed by reactions occurring as a result of compositing. For example, dissolved oxygen, pH, free carbon dioxide, dissolved metals and bacteria may all be changed by such reactions.

iii. In forming the composite sample, proper allowance must be made for the effect of variations in the flow rate of the water of interest during the time over which samples are collected.

iv. The uncertainty of the estimate of average quality from a composite sample will generally be worse than the estimate obtained by analyzing each of the individual samples. Thus, suppose σ_s represents the standard deviation of variations in true quality, and σ_a is the standard deviation of a single result due to analytical errors. The standard deviation of the mean result from the individual analysis of n samples is:

$$\sqrt{\frac{\sigma_s^2}{n} + \frac{\sigma_a^2}{n}}$$

The standard deviation of the result from one analysis of a composite from n samples (equal volumes of each sample) is:

$$\sqrt{\frac{\sigma_s^2}{n} + \sigma_a^2}$$

However, provided σ_a^2 is small compared to σ_s^2/n, compositing will have negligible effect on precision.

Another useful technique can be used to obtain, in effect, a composite sample. This consists in passing a stream of sample (continuous or intermittent) through a system (for example, an adsorbing column) that removes the determinand from the sample. The determinand is then subsequently recovered and measured. This technique is commonly used for removing organic compounds from very large volumes of water using activated carbon as the adsorbing material (100). This technique is capable of efficient concentration of many, but by no means all, organic compounds. Applications of this technique have recently been reviewed (100, 101). Care must be taken in applying this technique because bacteria grow on carbon filters thus consuming some organic compounds and producing others. Other adsorbents have been used, for example, ion-exchange resins (102–104) and activated alumina (105). Other examples of this general technique are: continuous evaporation for non-volatile impurities (75) and continuous centrifugation (106, 107) and filtration (108) for suspended materials. An approach using dissolved oxygen integrator devices has been reported (109) for obtaining the average dissolved oxygen content of a water over an extended time-period. In principle, any method of sample concentration capable of being applied on-line to a stream of sample may be used. Care may be required in the subsequent recovery and measurement of the determinand because interfering materials may also be concentrated.

4.7 Volume of Sample

The volume of sample collected is usually unimportant provided it is sufficient for all the required analyses, and enough remains to allow repeat analyses if required. When analytical methods involving preliminary concentration of the determinand in the sample are used, the sample volume may need to be increased if very small concentrations are to be measured. The volume required will normally be given in the analytical method and will not be discussed here. However the following points should be borne in mind.

i. When contact of the sample with air is to be avoided (for example, when determining dissolved gases, substances that react with air, pH and conductivity in waters of low conductivity) the sample container should be completely filled.

ii. When samples require vigorous shaking before taking portions for analyses (for example, for bacteria or undissolved materials), the sample container should not be completely filled. This allows the sample to be shaken before removing portions for analysis. This procedure may, however, be inconsistent with that in i. above in that contact of air may need to be avoided to prevent formation of undissolved materials in the sample when such materials are to be determined.

iia. The approach recommended then is that the sample bottle should be completely filled; but before the sample is taken a few pieces of clean, sterile inert solid such as solid beads or magnetic stirrerbar are put into the bottle. When portions are required for analysis, the bottle should be shaken in the usual way. How the sample is taken from the bottle will depend on the degree to which exposure to air can be tolerated. If the sample reacts rapidly with air, the sample can be taken using a piston pipette or syringe inside a well purged bag of oxygen free nitrogen, arrangement made for the replacement of the volume abstracted by a suitable immiscible unreactive liquid, or use made of inert plastic bottles that collapse as emptied.

iii. For small concentrations of determinands present as discrete particles (for example, undissolved materials, bacteria, algae), a minimum volume of sample may be needed to control errors arising from the statistical variations in the number of particles in a given volume of sample. For example if the water of interest contained 10 particles/litre, samples of 100 ml would not all contain 1 particle; some would contain none, some one, some two, etc. The relative variability of the number of the particles in the sample decreases with increasing sample volume.
Similar considerations apply to the area of a sediment sampled for benthos (see Section 4.8.5).

iv. In order to ensure adequate stability of different determinands between sampling and analysis it may be necessary to collect the total volume of sample required in several containers of different types and/or containing different preserving agents. This is discussed in Sections 4.8.3 and 4.9.2. The appropriate sample containers should be planned before any sample collection is attempted.

v. When the concentration of determinand in the water being sampled changes rapidly with time, the volume of sample collected may systematically affect the concentration in the sample. This can happen, for example, for lead in drinking water from a consumer's tap. On first opening the tap, the lead concentration may be relatively high but then often decreases so rapidly that the sample volume can markedly affect the concentration of lead in the sample.

4.8 Sample Collection

4.8.1 Manual sampling techniques

The choice of a correct technique for collecting samples is most important; otherwise, markedly non-representative samples may be obtained. Two main aspects are involved: the sampling system and its method of operation. These are discussed in Sections 4.8.1.1 and 4.8.1.2.

4.8.1.1 *Sampling systems*

The term 'sampling system' refers here to that device that is used to obtain a sample of the water of interest. Of course, the need for sampling systems is avoided when instruments or sensors capable of being directly immersed in the water of interest are used, for example, dissolved oxygen and conductivity probes. This is one of the principal advantages of in-situ analysis.

Certain determinands, for example, dissolved oxygen, require special sampling systems and/or techniques. These are described under the individual analytical methods and detailed description is not attempted here. It is essential, therefore, to read the analytical procedures in detail before choosing the appropriate techniques of sample collection. However, for many applications concerned with natural waters, no special sampling system is required. It is often sufficient simply to immerse a container (for example, a bucket) in the water of interest so that it fills with water which may then be poured into appropriate sample containers (see Sections 4.8.3 and 4.9.2). Alternatively, the sample containers may sometimes be directly immersed in the water though it may be advisable in many cases to avoid sampling of surface films. Care must be taken to ensure that neither the collecting nor the sample containers contain materials that may cause contamination of samples; this aspect is discussed in Section 4.8.3.

When it is required to sample from depths which prevent the use of such simple techniques, special containers are available for lowering into the water and obtaining a sealed sample from a chosen depth. Many such devices have been used, and a number are described in detail in references 23, 59, 60, 75, 99, 110–113. A useful review of such equipment for bacteriological examination of waters is given in reference 113. Two main types of depth samplers can be distinguished.

The first consists essentially of a tube with hinged, tightly-fitting lids at both ends. The tube is lowered on a cable into the water with both lids open; when the desired depth has been reached, a weight is allowed to drop down a cable so that it activates a spring mechanism which closes both lids. To ensure that the sample retained in the tube represents as closely as possible the water of interest, it is desirable to use samplers with no impediment to the flow of water through the tube while it is being lowered through the water.

The second type consists of a sealed container filled with air (or another gas if desired) which is lowered on a cable to the required depth. The means of sealing, for example, a rubber bung, is then released so that the container fills with water as the gas is displaced (see reference 188, figure 1).

The sampling device should be robust so as to withstand rough handling, and, if used to sample at great depth, to withstand high pressures. If the sampling device is to be used for bacteriological samples, it should be

capable of being sterilized and should be constructed of an inert material, that is, not exert a bacteriostatic or bactericidal effect as can happen with some metals or certain types of rubber. It may be preferable when taking bacteriological samples at depth to use a sterile sample bottle in the sampling device.

When sampling from treatment plant and distribution systems, and for certain applications for natural waters, a pipe or tube is inserted into the water of interest so that a stream of sample can be obtained when and where required. Such sampling systems have been described in detail (75, 76), and Mancy and Weber (114) have discussed certain aspects for industrial waste-waters. Sampling systems for natural waters such as rivers must be carefully selected and installed to avoid blockage of the inlet by debris in the water. It is usually necessary to protect the inlet by surrounding it with both a coarse and a fine mesh, and frequent inspection and removal of accumulated debris may be required. Sampling systems in exposed locations, for example, river-banks, may also need protection from vandalism and environmental effects such as temperature. When pumps are required to deliver a stream of sample, submersible rather than suction-type pumps should be used when dissolved gases are of interest. Suction may also cause increased concentrations of suspended solids. Contamination from pump components may also be a problem when trace metals are of interest. For such applications, peristaltic pumps using plastic tubing can be very useful. The need for pumps can also cause problems of installation when water levels fluctuate appreciably, for example, as in some estuaries and rivers. Mounting the pump on a floating platform has often been used to counteract this difficulty. Problems and errors may be caused by the growth of bacteria and/or algae in the tubing from the pump. These and related problems have been discussed by many authors (see, for example, references 75, 115 and 116). In view of the descriptions given in the references cited above, further discussion is restricted to aspects of general importance in any sampling system.

Isokinetic sampling – The concentrations of determinands in the water entering the sampling system should be the same as those in the water being sampled. There is usually no problem in ensuring this except when the determinands consist of undissolved materials with densities appreciably different from that of water. Such materials tend not to follow the streamlines of the water as it enters the sampling system, and their concentration may, therefore, be changed (116). To prevent this effect when sampling from a flowing stream of water, the rate of sampling should ideally be adjusted so that the velocity of water in the inlet of the sampling system is the same as that of the water being sampled, that is, iso-kinetic sampling. The importance of deviations from iso-kinetic sampling depends on several factors, but when undissolved materials are of interest it seems generally desirable to attempt to achieve approximately iso-kinatic sampling. For a similar reason, the inlet of the sampling system should face into the water-flow when undissolved materials are of interest. Thus, the common practice of simply joining the sampling pipe to the outside of the pipe being sampled is generally undesirable (75).

Effect of sampling system on concentrations of determinands – The concentrations of determinands in the sample must not change in passage through the sampling system. This desideratum may be prevented by several effects. Thus, the determinand may deposit within the sampling system, for example, undissolved solids may settle gravitationally onto the walls of the system, dissolved materials may be adsorbed. The determinand may also undergo chemical and/or biological reactions, for example, large proportions of ammonia can be oxidized by the action of bacterial films on the walls of samplers, dissolved oxygen can react with mild steel or copper sampling lines. In addition, the determinand may be released into the sample stream either from material adsorbed on walls (for example, dissolved oxygen can be released by respiring biological material) or from the materials of the sampling system itself (for example, contamination by metals or organic materials when metallic or plastic materials, respectively, are used). All these effects can be of great importance for sampling systems consisting either of a simple container or of a flow system.

Certain general precautions are useful in minimizing such effects, and in considering these aspects it is emphasized that a sampling system suitable for certain determinands is not necessarily suitable for others. Each determinand should be considered individually.

First, it is useful to minimize the contact-time between the sample and the sampling system. When sampling lines are used, they should, therefore, be kept as short as possible, and a high linear velocity of sample maintained through them (subject to the need for iso-kinetic sampling if required).

Second, the materials used for sampling systems should be such that no important contamination of sample occurs. Plastics are often suitable, particularly when trace amounts of metals are to be determined, though other applications may require metallic samplers, for example, for waters of high temperature and/or pressure or when small concentrations of organic compounds are to be measured. Stainless steel is often suitable for such requirements, and glass, though fragile, can be technically useful. Whatever the sampling system, it is generally desirable to check experimentally that it causes neither important contamination of samples nor any other type of bias.

Third, the sampling system should be kept adequately clean, particularly with regard to undissolved materials and biological films. Opaque sample lines are usually desirable for preventing algal growths, and regular flushing of the sampling system with a biocide can also be useful. Residual biocide should be well flushed from the system to avoid possible contamination. Simple design of sampling systems to ensure their cleanness; smooth surfaces and the absence of flow disturbances such as bends, stagnant areas, many taps and valves, are all likely to be advantageous.

4.8.1.2 *Collection of samples*

It is very important that the procedure to be used for collecting samples be carefully prescribed and followed; this is particularly true if the personnel involved are relatively unskilled scientifically. Collection of samples may involve hazards to the person sampling, and safety aspects are discussed in Section 4.3.

Contamination of the sample from the environment around the outlet of a sampling line can be of great importance when small concentrations of determinands are to be measured. The site should always be inspected so that possible sources of contamination can be eliminated, and contamination from the hands of the sampler should also be considered. Particular care is often needed to prevent contamination of bottle caps or stoppers while the bottles are being filled. Detailed recommendations for sampling for bacteriological analyses are given in reference 93, 99 and 113, and for biological analyses in reference 7.

When sampling from a boat or ship consideration must be given to possible contamination from the hydrowire and from the ship or sampling platform.

Contamination may also arise from the exhaust gases and airstream from helicopters.

Before collecting a sample, it is always desirable to allow the water to run to waste for a few minutes except when there is special interest in the quality during the first few minutes, for example, in sampling drinking water from consumers' taps. This reduces the possibility of contamination of the sample by materials that have deposited in the sampling lines. The flow conditions during sample collection should be standardized and kept constant until the required volume has been obtained; opening taps and valves during the sampling period is particularly to be avoided. It is often advantageous to maintain a permanent flow of sample through sampling lines even when it is not required for analysis.

Many authors recommend that sample containers be rinsed two or three times with sample before finally filling the container. This is a useful practice, but cannot always be adopted, for example, when the sample must be collected into a container with a preserving reagent (see Section 4.9.2) or when the sample contains materials that may be adsorbed on the walls of the container, for example, suspended solids, metals, oils and greases. In such cases, the containers must be adequately clean and free of water when they are taken to the sampling location.

Severe wintery conditions may cause problems. It is essential to ensure that any sampling devices and other equipment are working efficiently. Collection of samples for dissolved oxygen from ice-covered lakes must also be made with great care to prevent contamination of samples by air; sample bottles should also be completely filled and securely sealed so that oxygen is not lost from the sample as it warms up. Water from freshly melted ice should be avoided.

4.8.2 **Automatic sampling techniques**

A number of commercially-available devices allow a series of samples to be collected automatically, are often easily portable and may be used for any type of water. Two main types are available.

In the first, portions of the water of interest are collected at fixed time-intervals, each portion being of the same volume. The portions may be collected as required into one container or separate containers. Such equipment usually provides a choice of factors such as the number of samples in a given period, the duration of that period, the time during which each sample is collected, and the volume of each sample. These samplers are useful when concentration rather than mass of a determinand are of interest or when variations in flow rate of the water being sampled are negligible.

When the mass of a determinand is of interest and flow-rate varies appreciably, two approaches are possible. In the first, the automatic sampler is arranged to provide equal volume samples at a frequency directly proportional to flow-rate; in the second, the volume of sample collected at equal intervals of time is directly proportional to the flow. Both types may again arrange for each portion of sample to go into one container or into separate containers.

Many different designs of sampler have been described, and a number are made or marketed in many countries. Two review papers (98, 117) may be consulted for more details, and information is also given in references 25, 114 and 118–120. When considering the use of commercially-available automatic samplers, their suitability for the particular application should be critically assessed, for example, the flow-rates within sampling lines may be insufficient to prevent deposition of suspended materials.

Automatic samplers can be invaluable for many purposes, for example, preparing composite samples, studying variations in quality, obtaining samples at inaccessible locations. It is essential, however, to ensure that sample instability (see Section 4.9.2) does not lead to errors as a result of the longer storage time of samples entailed by automatic samplers. Preserving reagents may be added to the sample containers to ease this problem; alternatively, the containers can be installed in a refrigerated compartment when suitable preserving agents are not generally feasible, for example, as with biochemical oxygen demand.

4.8.3. **Sample containers**

4.8.3.1 *Factors affecting choice of sample containers*

Sample containers may have important effects on sample stability, and compilations of analytical methods often make specific recommendations on the type of container suitable for each determinand, though different publications do not always agree. A useful summary of the properties of many materials used for containing seawater is given in reference 121. Another publication (122) gives details of storage tests for different containers, and useful references to previous work.

Polyethylene or glass bottles are most commonly used, and both materials are often equally satisfactory. Other plastic materials (for example, polypropylene, polycarbonate) are used, but there is greatest experience of polyethylene. The ability to seal the bottles tightly with stoppers or caps is important. Glass bottles have the advantages that the condition of their internal surface is more readily apparent, and they can be more vigorously cleaned. For example, glass bottles can be sterilized by heating, and are, therefore, used for bacteriological samples. On the other hand, polyethylene bottles are less liable to breakage. Opaque sample bottles may be useful for reducing biological activity in samples.

As well as the factors mentioned in the preceding paragraph, sample containers should be chosen on the basis of three main considerations.

i. The material of the containers may cause contamination of samples, for example, sodium and silica can be leached from glass, organic substances can be leached from plastics.

ii. Determinands may be adsorbed on the walls of containers, for examples, trace metals by ion-exchange processes on glass surfaces, adsorption of benzene by plastics.

iii. Constituents of the sample may react with the container wall, for example, fluoride may react with glass.

These effects generally become more and more important as the concentrations of determinands become smaller. Thus, when determining larger concentrations of, for example, chloride, sulphate, nitrate, hardness, the type of container is usually unimportant. However, when determining small concentrations (say, less than 1 mg/l) of many determinands, the validity of the sample may be completely destroyed by these processes. It is essential, therefore, to ensure that appropriate containers are used

Some suggestions for containers and preserving agents for particular determinands are summarized in the Appendix, page 44.

4.8.3.2 *Contamination by sample containers*

As a general rule, glass bottles should be used when organic compounds are to be determined, and polyethylene bottles should be used for determinands that are major constituents of glass, for example, sodium, potassium, boron, silicon. Polyethylene is now generally favoured for trace concentrations of metallic impurities. Useful discussions of contamination effects are available (123, 124). In controlling contamination effects, a few particular points are worth bearing in mind.

i. It is not necessarily only the major components of container materials that cause contamination. For example, errors have been reported from iron, manganese, zinc and lead leached from glass, and from lithium and copper leached from polyethylene.

ii. Thorough cleaning of new bottles and bottles after use is essential. Chromic acid is often suitable for glass, and approximately molar hydrochloric or nitric acids can be used to clean polyethylene. Cleaning solutions containing determinands should generally be avoided, for example household detergents contain sufficient phosphate to cause contamination problems in its determination; chromic acid should be avoided when chromium is to be determined in samples. Experimental tests should be made on the bottles to determine whether or not any contamination of samples is satisfactorily small. Such tests can be made by placing high-purity water in each of the bottles, storing them as samples are to be stored, and analysing the contents of each bottle at the beginning and end of an appropriate test period. Bottle caps may contain inserts (for example, rubber, cardboard) that cause contamination. Generally it is best to use stoppers or caps containing only the material from which the bottles are made.

iii. The nature and magnitude of contamination effects may depend on the manufacturer of a particular type of container. Further, bottles of identical type from the same manufacturer may differ among themselves. It is sound practice, therefore, in trace analysis to check that each bottle to be used is satisfactory from the standpoint of contamination.

iv. The importance of contamination may depend on the sample; it is desirable, therefore, to check the effects for different types of sample. For example, the pH of a weakly-buffered water may be significantly affected by storage in a soft-glass bottle, while no important error would occur for a hard, well-buffered water. Hard-glass bottles are often preferable to soft glass because of the former's greater resistance to attack by aqueous solutions.

v. Another type of contamination may arise when polyethylene bottles are used. Certain volatile substances diffuse, albeit rather slowly, through the walls of the bottles (125). Thus, contamination by the gases in the air around the bottles or losses of volatile substances (for example, mercury) from the samples may occur even though in practice these effects seem not usually to be important. The use of high-density polyethylene substantially decreases the effect.

4.8.3.3 *Adsorption of determinands by containers*

Sample containers may also cause errors by adsorption of determinands. Trace metals are particularly liable to this effect, but other determinands (for example, detergents, pesticides, phosphate (126)) may also be subject to error. The degree of adsorption depends on many factors including the nature and concentration of impurities in the sample, the material and history of the container, and temperature: The addition of preserving reagents (see Section 4.9.2.4) is probably the best general approach to avoiding problems. However, even when such reagents are used, it is always preferable to make experimental checks that adsorption effects are tolerably small. Studies of adsorption effects are given in references 112, 127 and 128. Some metals (for example, mecury and silver) are particularly liable to losses to the walls of the containers.

4.8.4 **Filtration of samples**

It is often necessary to distinguish between dissolved and undissolved forms of determinands, for example, metals or phosphorus. When filtration of the sample is used to separate the two forms, it is usually important to filter the sample during or immediately after collection, otherwise changes in the proportions of the two forms may well occur during the period between sampling and filtration. This need for early filtration will often necessitate filtration of samples before they are taken to the Laboratory. Simple techniques for filtering samples through membrane or glass-fibre filters have been described (111, 127, 129). Filtration immediately after sample collection may also be required as a sample preservation technique (see Section 4.9.2.2).

Any equipment used for sample filtration should be carefully cleaned and tested to ensure that it does not cause important contamination of samples or marked changes in pH value because of loss or gain of carbon dioxide; filtration under pressure rather than suction is generally desirable. It is important to ensure that impurities leached from the filter do not cause important contamination; extensive pre-washing of the filter is sometimes required to prevent this effect (111, 112, 130, 131).

In considering the use of filtration, possible losses of dissolved determinands by adsorption on the filter and

filtration system should be considered (132); see also Section 4.9.2.2).

4.8.5 **Sediment sampling**

Two main objectives are included under this heading. In the first, the primary purpose is to obtain a representative sample of the biological population of the sediment; in the second, a sample of the sediment itself is required. Which of these objectives applies will govern the type of sampling device to be used.

Many different types of bottom and sediment may be encountered, and almost as many sampling devices have been described and used. The topic is rather specialized, and is dealt with in more detail in other publications in this Series. The aim of the present section is, therefore, simply to indicate the types of sampling devices available, the considerations involved in selecting from among them, and references to more comprehensive descriptions of such devices.

In shallow waters or when sediments are exposed, hand sampling may sometimes be all that is necessary. In other circumstances, some specific form of sampling device will be required. As stated above, the precise purpose of the sample will affect the choice of device, and this is also affected by the nature of the bottom and sediment, and the particular position on or in the sediment of interest. For example, a rocky bottom may prevent the use of certain types of dredge samplers (see Section 4.8.5.1), while the need to sample sediments in depth may dictate the use of a core sampler (see Section 4.8.5.3). Three main types of sampling device can be used, and they can be summarized as follows. More detailed descriptions are given in references 7, 99, 113, 133 and 134.

4.8.5.1 *Dredge samplers*

These usually consist of a hollow vessel, open at one end and closed at the other. The vessel is lowered to the bottom on a cable, and then dragged along with the open end leading, the material from the bottom being retained in the closed end. When the area of interest has been covered, the dredge is brought back to the surface for collection of the sample. A mixture of bottom sediments is collected over an area and at varying depths. It is possible that sediment particles are washed out of the open dredge as it is brought up through the water. Dredges are best suited for collecting samples of coarser sediments, particularly gravels and shells. Strengthened dredges can be used to obtain samples of rock deposits.

4.8.5.2 *Grab samplers*

These consist of a vessel with a set of jaws that is lowered on a cable to the desired position on the bottom. The jaws are closed so that a sample of bottom materials is taken and retained with the vessel which is then returned to the surface.

The majority of grabs are constructed to collect a fixed area of sea bed typically 0.1 m^2 in order to determine animal numbers. They are large and heavy, and consequently require proper handling and hauling facilities. Lowering is usually by wire held away from the side of the boat by a boom which allows the grab to drop vertically through the water. Boat movement, due to wind and wave action, and strong currents cause problems. The grab may close prematurely, or land at the wrong angle so that no sample is collected.

Grabs are best suited to sampling coarse silts and fine gravels, but penetration into compacted sands is usually poor. Pebbles and shells can prevent the jaws from closing which results in loss of sample.

4.8.5.3 *Core samplers*

These consist simply of a tube which is pushed into the sediment to the desired depth. On retraction of the sampler, a core of the sediment is obtained in the tube, various arrangements being used to ensure that the core is retained as the sampler is brought back to the surface. Core samplers may be either free-falling or power-assisted. Core samplers are best suited to collecting samples of fine deposits. Once back on the surface, the core can be cut into suitable lengths for subsequent analysis.

4.8.5.4 *Artificial-substrate samplers*

These samplers are used in the biological field, and consist of a number of units (for example, a series of plates) on which organisms may grow. The samplers are placed on the bottom at the point of interest, and can be retrieved for examination when desired, thus overcoming many of the problems encountered in direct sampling. Such samplers also have disadvantages, mainly that they differ from the natural environment. Their use has been recently reviewed and compared with other sampling techniques (7, 135).

4.8.5.5 *SCUBA divers*

When the aims of the sampling programme justify it, the money is available, and the environmental conditions (that is, visibility and especially depth) are suitable free-swimming divers equipped with self-contained underwater breathing apparatus (SCUBA) may be employed to collect bottom deposits. Divers can take surface samples of the sediment, including the surface 'floc' directly into glass bottles, and also push small corers into the sediment. They are particularly useful when information about the accretion of sediment over a period of time is required, provided that precise positions marked on the bottom can be easily located.

The limitations of divers are as follows:

i. available work-time reduces with increasing depth;

ii. costs may be considerable in relation to the quantity of work carried out – for safety reasons the usual minimum is a three diver team with only one working.

iii. considerable safety precautions are necessary;

iv. identification of sampling position can be difficult;

v. data recording underwater is difficult.

4.9 Sample Transportation and Storage and Sample Preservation Techniques

Due to the complex and unstable nature of many water samples, it is almost always advisable, and in many cases essential, that samples be analysed as soon as possible after their collection. However, immediate analysis is often impossible or inexpedient, and so the methods of sample transportation and storage as well as the need for adoption of sample preservation techniques must be given very careful consideration.

4.9.1 Sample transportation and storage

The transportation of samples should be arranged, both with regard to speed of transport and convenience of their reception at the laboratory, so that analysis can be commenced as soon as possible after the samples were collected. Special facilities may have to be allocated for sample transportation as and when necessary; for example special vans or cars will often be essential when samples from large geographical areas are to be taken to a central laboratory. Facilities for the refrigeration, or even freezing, of samples during transport may also be valuable. When samples cannot be brought to a laboratory sufficiently rapidly, the use of mobile laboratories or on-site analysis for particularly unstable determinands, (for example, bacteria, biochemical oxygen demand) should be considered. The best solution to sample transportation problems needs to be decided for each application.

Samples should be transported and stored at temperatures not above those at which they were collected. Care must be taken with the handling and packing of sample containers to ensure that they are not mislaid, broken or contaminated during transportation. The general precautions are fairly obvious, but special care should be taken to prevent contamination of the outside of the sample containers, particularly round their necks and stoppers. Under extreme conditions in winter, samples may freeze, which could lead to breakages if they are kept in glass containers. Undue agitation or exposure to light during transport should be avoided.

On arrival at the laboratory, similar precautions to those adopted in transportation should be taken to prevent loss, breakage or contamination of the samples. A separate, clean store-room, in which no chemical reagents are used, and which can be kept dark and cool, should be provided for the storage of samples before analysis. Facilities for the refrigeration of samples should be available, and a refrigerated store-room would be ideal in most cases.

4.9.2 Sample preservation techniques

A vital consideration in sample transportation and storage is in ensuring, as far as possible, that the concentrations of the determinands in the sample do not vary between the time of sample collection and the time of analysis. Unfortunately, this aspect of sampling is frequently accorded insufficient attention. Despite the optimization of transport arrangements and storage facilities, a time interval ranging from a few hours to several weeks will in most cases elapse between sampling and analysis. Many chemical, physical and biological processes can lead to marked changes in the composition of samples, even over a short period of time, and if no precautions are taken the sample on analysis may be quite unrepresentative of the water body at the time of sampling. There are very few determinands which are not subject to this problem. Examples of the processes involved are given below.

i. Biological species, (bacteria, algae and other organisms) can have several effects on the composition of samples. They can consume or modify the chemical form of certain determinands or themselves produce new substances.

   Determinands which are affected by these biological processes include dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, total oxygen demand, total organic carbon, carbon dioxide, hardness, alkalinity, pH, organic compounds, nitrogen compounds, phosphorus compounds, silicon compounds, and phenols. The effects of biological processes are normally more serious for samples associated with sewage, sewage effluents, microbiological effluent-treatment plant, and heavily polluted rivers downstream of effluent discharges than in samples of fresh and treated waters. The effects may be particularly serious in waters containing low concentrations of nutrients.

   Biological changes taking place in a sample may change the oxidation state of an element. Soluble compounds may be converted to organically-bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

ii. Some determinands can be oxidized by dissolved oxygen in the samples or by oxygen from the air: for example, organic compounds, ferrous iron, iodide, cyanide, sulphide.

iii. The absorption of carbon dioxide from the air may affect some determinands: for example, pH, conductivity, alkalinity, carbon dioxide, hardness.

iv. Some determinands may be precipitated (for example, metallic compounds including calcium carbonate, magnesium phosphate and aluminium hydroxide) or volatilized (for example, oxygen, cyanides).

v. Adsorption on to the surfaces of the sample container or on to solids in the sample can affect dissolved and colloidal metals and some organic compounds.

vi. Polymeric materials can depolymerize (for example, condensed inorganic phosphates (136) and polymeric silicic acid (137)) or simple compounds could polymerize.

vii. Colour, odour, and turbidity may change.

As well as being dependent on the chemical, physical and biological characteristics of the sample, the extent of such processes is also influenced by the conditions under which the sample is handled: for example, temperature, exposure to light, the composition and dimensions of the sample container, and agitation during transport. Obviously one of the most important factors is the time between sampling and analysis, and it should be emphasized that these processes can take place sufficiently rapidly to alter the composition of the sample seriously within a few hours. The effects of these reactions are usually more pronounced when the concentration of the determinand is small. Thus, the rate of change in the concentration of a given determinand can vary from one type of water to another, and from time to time for the same body of water.

Many investigations of the stabilities of different determinands have been made for various types of water, and several methods of sample preservation have been suggested to prevent changes in sample composition. However, it must be emphasized that complete sample preservation is practically impossible, and that preservation techniques can normally only retard the processes which occur. The conclusions reached from the investigations of the use of preservation techniques do not always agree, and this is not surprising considering the complexity and number of processes possible. The main techniques which have been recommended for sample preservation are outlined below, but in view of the large number of reported investigations, a complete survey has not been attempted. Although the different preservation techniques are discussed individually, the best preservation is often obtained by using several of the methods together: for example, addition of a preserving reagent and refrigeration.

4.9.2.1 *Special storage conditions*

*Refrigeration** – The storage of samples in the dark at low temperatures (normally about 4°C) is a useful and widely employed method of sample preservation. At these temperatures, biological activity is significantly reduced or even completely prevented. Ideally the sample should be refrigerated immediately on collection, especially when the determinands are particularly unstable. Some examples of the use of this technique are given in the Appendix, page 44; it is often worth using as a minimum precaution when the stability of determinands in the sample is unknown.

Changes may also occur in sediments and sludges between sampling and analysis, and refrigeration at 2–4°C is often of value in preventing or reducing such effects.

*Freezing** – Freezing of samples in polyethylene bottles immediately on collection and storage in deep-freeze units at temperatures of about – 20°C has been suggested for several determinands and different types of water. However, this method of sample preservation may be difficult to arrange, particularly the immediate freezing of the sample. Analysis of the thawed sample must be commenced before any changes in composition can occur, and repeated freezing and thawing of the sample should be avoided. The advantages of freezing as a method of sample preservation are that the introduction of additional reagents is avoided and disturbance of the original speciation of many substances appears to be minimized.

Freezing has been recommended for the storage of sea water samples for periods up to several weeks for the determination of nitrogen, phosphorus and silicon compounds (138) and metals. The preservation of these and other determinands including biochemical and chemical oxygen demands has been reported with reasonable success for effluents and waste waters (139–149), estuarine waters (150) and fresh waters (111, 151) although in some cases the results for biochemical oxygen demand were low. However, other investigators have reported errors when silicon compounds (137) or phosphate (152–154) are to be determined. The use of freezing for the preservation of suspended solids generally produced high results (144, 147). Rupture of cells of biota on freezing is another possible disadvantage of this technique.

4.9.2.2 *Immediate treatment of the sample*

Filtration – Biological activity in the sample can be greatly reduced by filtering the sample through a filter of small pore size on which algae and bacteria are retained. Membrane filters (pore size about 0.5 μm) or glass-fibre filters are suitable for this purpose. Care must be taken to ensure that materials from the filter are not leached into the sample and cause contamination, and extensive pre-washing of the filter may be necessary (111, 130, 131). Contamination from membrane filters prior to organic carbon determination has been reported (155–157). Consistent differences can occur between the leachable metal contents of filters from different suppliers. For some purposes, the use of glass-fibre filters is preferable even though their pore sizes are less well defined. They have the advantage that they can be heated at sufficiently high temperatures to remove organic material and volatile metals such as mercury. Obviously, filtration cannot be used for determinands which may be wholly or partially retained on the filter or filtration apparatus.

In addition to the need to reduce rapidly biological activity, filtration should be carried out during or immediately after sample collection since changes in composition on storage may be accelerated by the additional surface area presented by particulate material. Furthermore, initial treatment to preserve samples will tend to alter the distribution between phases. For example, disruption of cells of plankton on freezing can lead to subsequent release of cellular contents to solution. Vacuum or pressure filtration is required because of the small pore size of the filters used, and suitable apparatus for on-site filtration has been described (111, 127, 129).

Filtration has been recommended for the preservation of several determinands, particularly phosphorus and silicon compounds (99, 152, 154, 158). Filtration through a membrane filter has also been recommended when dissolved rather than suspended or total forms of a metal are to be determined (159–161). For this purpose, in addition to the general precautions mentioned above, it will often be necessary to standardize the type of filter used due to the empirical and incomplete separation of dissolved and undissolved forms of metals; otherwise, the comparability of, and the ability to draw conclusions from, results may suffer. To emphasize the empirical nature of the technique the term 'filtrable' has been suggested (99) in place of the more usual 'soluble' or 'dissolved'. The effective cut-off in particle size for a filter of specified pore diameter will also vary with clogging of pores which depends on the volume filtered and the particulate load. Cellulose-ester membrane and glass-fibre filters will under many conditions retain particles much smaller than the specified pore size (162).

Dissolved metal ions may also be absorbed onto the filter if unacidified samples are filtered (132). Changes in pH because of loss or gain of carbon dioxide during filtration should be avoided; otherwise, metallic compounds may dissolve or precipitate.

Other treatment – In some cases it may be possible to commence the analysis of the sample at the time of collection, so that the determinand is converted into a more stable form, the analysis being completed later. This approach may be adopted with the Winkler method for dissolved oxygen (23, 158), when the addition of the manganous sulphate and alkaline iodide-azide reagents leads to the formation of the oxidized manganese precipitate which is stable for several hours. This procedure is described in greater detail in another publication in this series (see reference 188).

* Never freeze water samples in glass bottles. They burst.

4.9.2.3 *Special Sample containers*

Sample containers have already been discussed in Section 4.8.3. However, the following points are relevant to sample preservation.

Normally, polyethylene or glass bottles are used for sample storage, and many publications contain recommendations on which type of bottle should be used for particular determinands. These recommendations do not always agree, and the current views of the Standing Committee of Analysts are summarized in the Appendix.

Dark brown or opaque bottles are generally useful for reducing biological activity. An interesting approach has been reported (163) when small concentrations of orthophosphate are to be determined. It was found that bacteria on the surfaces of polyethylene bottles caused significant changes in the phosphate concentration. This could be overcome by treating the bottles with an iodine-potassium iodide mixture before use. The iodine adsorbed by the polyethylene acted as a biocide and retained its efficiency for long periods; the bottles could, therefore, be used many times without further treatment.

For determinands such as oils, greases and organochlorine pesticides, it may be virtually impossible to prevent adsorption on to the surfaces of the sample container. Therefore, it is necessary to reserve sample containers solely for that particular determinand so that the adsorbed material can be removed from the container (for example, by solvent extraction) as part of the analytical procedure.

Normally, it is possible to re-use containers several times provided they are appropriately cleaned between each use. The cleaning procedure must be chosen depending on the type of container and the nature of the sample and the determinand (see Section 4.8.3). With extensive use, chemical or biological deposits may build up slowly on the walls of containers, and it must be ensured that this does not reach the stage where errors arise. From this point of view, glass bottles are preferable to plastic ones because the condition of their walls is more easily inspected.

4.9.2.4 *Addition of preserving agents*

Satisfactory stability of many determinands can often be achieved by the addition of a chemical reagent to the sample immediately on collection or preferably, whenever possible, by the addition of the reagent to the empty container before collection of the sample. When this is feasible, the use of preserving reagents is of great value and often the simplest approach to sample preservation, especially when one reagent will stabilize a number of determinands.

When preserving reagents are used, they may interfere with the analytical method. Thus, both the preserving reagent and the analytical method should be considered together, and tests made to check their compatibility if any doubts exist. The preservative may also affect the chemical or physical forms of materials. For example, acidification of samples can lead to dissolution of colloidal and particulate metals, phosphates, etc, resulting in invalid data for these determinands. Thus, when dissolved metals are to be separated from undissolved by fiiltration and then determined in the filtrate, the samples must first be filtered, and then the filtered sample acidified (159, 160, 164).

It is normally preferable to use relatively concentrated solutions of preserving reagents so that only small volumes need to be added to the sample. Corrections for the dilution of the sample by the preserving reagent will then be small or negligible.

Many different preserving reagents have been proposed, often in very different concentrations, and the conclusions reached on the suitability of preserving reagents are often conflicting.

Acidification of samples has been found satisfactory when trace metals are to be determined (12, 99, 110–112, 158–161, 164–167), but different acids and concentrations have been recommended. The minimum acidity required for stability depends on the metal to be determined, but the addition of sufficient nitric or hydrochloric acid to give a concentration of 0.05 to 0.1 M in the sample after collection seems fairly normal. However, 0.1 M to 0.3 M has been recommended when mercury (165, 166), or silver (167) are the determinands (see also reference 164 for silver). More recently, the addition of dichromate as well as acid for preservation of mercury has been preferred (168–170).

Biocidal reagents may be useful when the determinands are subject to biological reactions, for example, organic materials and compounds of nitrogen, phosphorus and silicon. Chloroform and certain other organic reagents (for example, formaldehyde, thymol) have been used in the past, but it now appears that these are not very effective (99, 140, 150, 152, 171–175), and the use of mercuric chloride or mineral acids is now more often reported (99, 111, 140, 158, 159, 171–173). Mercuric chloride, usually in concentrations of 20 to 40 mg $HgCl_2$ per litre of sample, is often recommended for preserving nitrogen compounds, while acid, normally 1 to 2 ml sulphuric acid per litre of sample, is used for determinands such as chemical oxygen demand, oils and greases. If mercuric chloride is used as a preservative, care is essential to avoid contamination of samples requiring mercury determination and to ensure safe disposal of samples after analysis because of the toxicity of the preservative. Special care is required for phosphorus because ortho-phosphate and other determinands are released when certain biological species are killed (152). However, this problem can be reduced by filtration of the sample before addition of the preserving reagent; see Section 4.9.2.2.

Many papers have been published on comparison of preservations; useful discussions of this topic appear in references 140, 150, 152, 163, 176–183.

In addition to preservatives suitable for a number of determinands, special preserving reagents for specific determinands may often be necessary, for example, copper sulphate and phosphoric acid for phenolic compounds (99, 158, 164), sodium hydroxide for phenolic compounds (158) and cyanide (158, 159, 164), and zinc acetate for sulphide (158, 159).

Given all the factors that may affect the stability of a determinand between sampling and analysis, it is difficult for many unstable determinands to recommend unreservedly any one preservation technique as universally suitable. However, an attempt has been made in the Appendix to this Chapter to tabulate, for each of a number of determinands, the type of sample container and preserving reagent (or other preservation procedure) thought likely to be of value for a wide range of samples.

Although this section is not primarily concerned with biological examination of samples, it is stressed that many biological species may show rapid changes in number between sampling and analysis. it is, therefore, usually important to take all possible steps to ensure that examination of samples begins as soon after collection as possible. The detailed recommendations given in the methods for biological examination should be consulted.

4.10 Sub-sampling from the Sample Container

Taking the portion for analysis from the sample container is generally straightforward except when undissolved materials are present. Several precautions are then usually necessary (see Section 4.7).

4.11 Data Collected with Each Sample

Sample containers must be clearly and unambiguously identified so that subsequent analytical results can be properly interpreted. Generally, it is desirable that all details relevant to the sample are recorded on a label that is attached to the sample container. When many sample containers are needed for any one sampling occasion, it will usually be more convenient to identify the containers by a code number, and to record all relevant details on a special form. Labels or forms must be completed at the time of sample collection. Sufficient information should be recorded so that the general condition of the water being sampled is clear. Recommendations on the minimum data required for surface and ground-water samples have been given by Rainwater and Thatcher (12). Coyne *et al.* (152) have suggested that a number of other details concerning the methods of sampling and preservation and the analyses required should also be recorded. It is especially important to record full details, including sample site location, when submitting a sample of anomalous material, taken as part of a statistical or routine survey. See Reference 186, part A, section 11.

4.12 References

4.12.1 Related publications

References 184 and 186 are related publications in this series. Several more similar specific sampling booklets are either in preparation or planned. Some methods booklets (for example reference 188) also contain detailed sampling information.

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Appendix to Chapter 4

A.4.1 Summary of Sample Containers and Storage Conditions for Waters and Effluents

The discusssion in Section 4.9 has stressed that it is vital to take all possible precautions to ensure that the concentrations of determinands in samples do not change by important amounts in the period between sample collection and analysis. The discussion also emphasized the many variable factors that may affect such changes. At present, there is insufficient knowledge to allow recommendation of simple-handling procedures that will unquestionably eliminate these changes for all determinands in all types of sample. Nevertheless, in view of the importance of this topic, a summary has been given below, for each of a number of determinands, of sample containers and storage conditions considered to be of common value. Whenever possible, these details have been obtained from the other Working Groups and Panels of the Standing Committee of Analysts considering analytical methods for particular determinands. When these Groups and Panels have not yet considered a determinand in detail, the following suggestions have been based largely on published information and relevant references are quoted. As the detailed analytical methods for further determinands are considered and published, their recommendations on sample containers and storage conditions may differ from the suggestions below because of advances in knowledge. *In this situation, it is emphasized that the recommendations in the published analytical methods take precedence over those given here.* It is also emphasized that the storage conditions quoted in the following table are not intended to cover all circumstances and may vary with the form in which the determinand is found, and with the sample type; the individual methods should be consulted for information on the suitability of less stringent conditions or the need for greater stringency.

Finally, a highly critical approach to the selection and use of sample containers and storage conditions is urged. To the maximum extent possible, tests of the efficiency of the selected procedures should be made on samples whenever there is doubt on the stability of one or more determinands. Perusal of Section 4.9 will help to identify possible important factors and to suggest alternative procedures if those selected initially are found to be inadequate.

Summary of sample containers and storage conditions for waters and effluents

(Note: The use of mercury compounds as preservatives is not recommended)

Determinand	Container (a) (P = polyethylene G = borosilicate glass)	Storage Conditions (b)	Reference (k) (p) (see section 4.12)
Acidity	G	Fill bottle to leave no air space. Store in cool, dark place. (q)	99,159
Alkalinity	G	Fill bottle to leave no air space. Store in cool, dark place. (q)	99,159
Aluminium	P	Add 20 ml 5M HCl/litre of sample.	
Ammonia		See nitrogen.	
Arsenic	P or G	Add 2 ml 6M HCl/litre of sample.	
Biochemical oxygen demand (c)	G	Fill bottle to leave no air space. Store at 4°C in dark. (q) (r) (s)	
Boron	P or soda glass	No special conditions needed.	
Bromide	P or G	Store at 4°C out of direct sunlight. (r)	159
Cadmium	P	Add 2 ml 10M HCl/litre of sample.	
Calcium	P	Add 2 ml 5M HCl/litre of sample.	
Carbon dioxide free (c) (o)	G	Analyze on site or fill bottle to leave no air space. Store at a temperature lower than that of the sample initially. (q) (s)	99
Chemical oxygen demand	G	Store at 2 – 5°C or add H_2SO_4 to give a pH of 1– 2. (n) If 'dissolved' COD is required, filter before storage. (d)	
Chloride	P or G	No special conditions needed.	
Chlorinated hydrocarbons	G	See note (e).	
Chlorine			
– combined (c) (o)	G	Analyze immediately after sampling.	189
– free (c) (o)	G	Analyze immediately after sampling	189
– total organic	G	See note (e).	
Chromium	P	By AAS – 2 ml/litre of sample. 50% (V/V) HCl by spectrophotometry – 2 ml/litre of sample. 30% (V/V) diluted HNO_3 (d_{20} 1.42).	
Cobalt	P	Add 2 ml 50% (V/V) HCl/litre of sample.	
Colour	G	Store in cool, dark place.	
Conductivity electrical	P	Fill bottle to leave no air space. Store at 4°C. (q) (r)	
Copper	P	Either 2 ml 50% (V/V) HCl/litre of sample or 1 ml HNO_3 (d_{20} 1.42)/litre.	
Cyanide (o)	P or G	Add NaOH to give a pH >12. Store in dark at 4°C. If oxidizing agents are present, it may be useful to add ascorbic acid. (n) (r)	99,159
Detergents			
– anionic	P or G	Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C. (r)	
– cationic	P or G	Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C.(r)	
– non-ionic	P or G	Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C. (r)	
Dissolved oxygen (c) (o)	G	Fill bottle to leave no air space. Analyze on site or 'fix' sample by adding manganese and alkaline iodide-azide reagents, then store in dark at 10 – 20°C for no more than 24 hours. (q) (s)	188
Electrical conductivity	P	Fill bottle to leave no air space. Store at 4°C. (q) (r)	
Fluoride	P or G	No special conditions needed.	

Determinand	Container (a) (P = polyethylene G = borosilicate glass)	Storage Conditions (b)	Reference (k) (p) (see Section 4.12)
Free carbon dioxide (c) (o)	G	Analyze on site or fill bottle to leave no air space. Store at a temperature lower than that of the sample initially. (q) (s)	99
Greases and oil	G	See note (e).	
Hardness (Total by EDTA)	P or G	No special precautions.	
Hydrocarbons (o)	G	See note (e).	
Iodide	P or G	Store at 4°C out of direct sunlight. (r)	159
Iron (o)	P	Add 20 ml 5M HCl/litre of sample. (t)	
Lead	P	Add 2 ml 5M HCl/litre of sample.	
Lithium	P or G	No special conditions needed. (f)	99
Magnesium	P	Add 2 ml 5M HCl/litre of sample.	
Manganese	P	Add 20 ml 5M HCl/litre of sample. (t)	
Mercury			
– saline samples	G	Add 20 ml 4.5M H_2SO_4/litre of sample.	
– non-saline samples	G	Add HNO_3 to give a pH of 1, and sufficient $K_2Cr_2O_7$ to maintain excess until analysis starts. (n)	
Metals (g)			
– total	P (m)	This depends on the method used and the metals expected to be present. The usual preservative treatments are either to add 20ml of 5M HCl/litre of sample, or to add 2–10 ml HNO_3/litre of sample: but be guided by the conditions for the most sensitive metal likely to be present. If necessary take two or more samples where preservation techniques are incompatible. If the sample is liable to react with air see notes (s) and (t).	159 (1)
– total filtrable	P	Filter on site (d) and add 2 – 10 ml HNO_3/litre of filtrate.	159
Nickel	P	2 ml/litre of sample 50% (V/V) HCl.	
Nitrogen			
– ammoniacal (c) (o)	P or G	If both free and combined ammoniacal nitrogen are required, fill bottle to leave no air space. If only total ammoniacal nitrogen is required, add HCl or H_2SO_4 to give a pH of 2. (n) Store at 4°C. (q) (r)	
– hydroxylamine (c) (o) hydrazine (c) (o)	P or G	Fill the bottle to leave no air space. Store at 4°C. (q) (r) (s)	
– kjeldahl (c) (o)	P or G	Unless free ammoniacal nitrogen is also required add H_2SO_4 to give a pH of 2. (n) Store at 4°C. (r)	159
– nitrate (c)	P or G	Store at 4°C. (r)	
– nitrite (c)	P or G	Store at 4°C. (r)	
– organic (c) (o)	P or G	Unless free ammoniacal nitrogen is also required add H_2SO_4 to give a pH of 2. (n) Store at 4°C. (r)	99
Odour (c) (o)	G	Fill bottle to leave no air space. Store at 1 – 5°C. (q) (r)	
Oils and greases	G	See note (e).	
Organic carbon total	G	Fill bottle to leave no air space. Sample preservation is dependent on the method used. Store at 4°C. For some methods addition of HCl to give a pH of 1–2 is required, for others the use of hydrochloric acid is barred. (q) (r) (s)	
Organic chlorine total	G	See note (e).	
Organo-chlorine pesticides	G	See note (e).	

Determinand	Container (a) (P = polyethylene G = borosilicate glass)	Storage Conditions (b)	Reference (k) (p) (see Section 4.12)
Organo-phosphorus pesticides	G	Immediately after sampling, add solvent to sample, shake, and store in spark-proof refrigerator at 4°C. (n)(r)	
Oxygen demand			
– biochemical (c)		Fill bottle to leave no air space. Store at 4°C in the dark. (q) (r) (s)	
– chemical	G	Store at 2 – 5° or add H_2SO_4 to give a pH of 1 – 2. If dissolved COD is required, filter before storage. (d) (n) (r)	
– total	G	Store at 4°C.(r)	
Oxygen dissolved (c) (o)	G	Fill bottle to leave no air space. Analyze on site or fix sample by adding manganese and alkaline reagents, then store in dark at 10–20°C for no more than 24 hours. (q) (s)	188
Permanganate value	G	Add H_2SO_4 to give a pH<2. (n)	
Pesticides organo-chlorine	G	Store at 4°C. (r)	
Silver	G	These are highly dependent on the method of analysis used subsequently. If cyanogen iodide or similar reagent is subsequently added to the sample, no special preservative addition should be made, otherwise an addition of HNO_3 to give a final concentration of 0.1–0.3M has been suggested.	167
Sodium	P	No special conditions needed.	99
Sulphate	P or G	Store at 4°C. (If sulphide and/or sulphite present, fill bottle to leave no air space). (q) (r)	
Sulphide (o)	P or G	Fix sample by adding zinc acetate and sodium hydroxide reagents on site. (n)	
Sulphite (o)	P or G	Fill bottle to leave no air space. Store at 4°C. (r) (s)	159
Solids			
– dissolved	G	No special conditions needed.	
– separable	G	No generally-suitable procedure. Analyze as soon as possible.	
– suspended (c)	G	No generally-suitable procedure. Analyze as soon as possible.	
– total	G	Store at 4°C. (r)	
Turbidity (c)	G	No generally-suitable procedure. Analyze as soon as possible.	
Zinc	P (m)	Either 2 ml/litre of sample 50% (V/V) HCl or 1 ml/litre of sample HNO_3 (d_{20} 1.42).	