

HYDROLOGICAL PROCEDURE NO. 2

WATER QUALITY SAMPLING FOR SURFACE WATER



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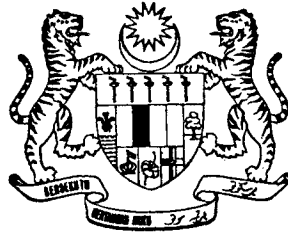
**WATER QUALITY SAMPLING
FOR
SURFACE WATER**

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WATER QUALITY SAMPLING FOR SURFACE WATER

1. INTRODUCTION

This publication sets out guidelines for the sampling of surface waters. The general principles involved in chemical and bacteriological sampling of streams, rivers, lakes and ponds are discussed, and specific recommendations on procedures for storage and preservation of samples are given. Groundwaters, suspended sediments and biological analysis are not considered.

Although written for organisations involved in routine water quality work, the guidelines set out herein do not eliminate the need for field staff experienced in water sampling. Where organisations have no such experience, they should discuss the proposed sampling programme with experienced and qualified staff. Organisations that have such staff include:

Drainage and Irrigation Department.

Chemistry Department.

Soil Section, Agriculture Department.

Adequate laboratory facilities must be available. Without them, reliable and accurate analyses of the chosen constituents cannot be obtained.

2. DEFINITION OF THE PROBLEM

There are four basic situations likely to require a sampling and analysis programme:

(a) checks of compliance with effluent quality and quantity requirements.

(b) an observed deterioration in water quality:

- viz by sight*
- (1) Oil and grease.
 - (2) Dead animals and/or plants.
 - (3) Excessive plant growth.
 - (4) Discolouration of the water.
 - (5) Absence of any life.
 - (6) Excessive sediments,

- by smell*
- (7) Sulphide.
 - (8) Sewage.
 - (9) Decomposing matter.
 - (10) Specific chemicals or wastes.

by touch (11) Thermal pollution.

(c) checks on the dispersal and effects of effluents on receiving waters.

(d) a need to monitor changes (if any) occurring either with time, or with position, in a body of water.

Clearly, the sampling and analysis programme must be designed to meet the requirements of the situation.

3. PLANNING (Choice of site, time and frequency of sampling etc.)

There will be occasions when a deterioration in water quality results from a single unexpected discharge of a pollutant to a water. Under these circumstances, any delay lessens the chance of identifying the nature and source of the pollutant, and anything other than the most superficial planning cannot be considered. The investigator must take samples as quickly as possible, using his initiative to make allowance for the rate of flow of the water, and record not only every detail which may be relevant to the discharge, but also details of the samples and sampling points. Within reason, safety lies in numbers of samples taken from all sites which may have received the pollutant. Analyses must be arranged without delay.

However, sufficient time will generally be available to seek expert advice in planning a sampling and analysis programme. This should include advice on possible causes of deterioration in water quality, means of establishing these causes, the species most useful and relevant for monitoring the quality of the water, selection of sampling sites, frequency and time of sampling and any special precautions necessary. Information on the following will assist in planning the most efficient investigation :

- (a) past and present quality of the water in question,
- (b) an adequate description of the relevant local conditions,
- (c) water flows and volumes,
- (d) sources, types and quantities of effluents,
- (e) usual events, such as the weather, excavations or new processes producing effluents,
- (f) the laboratory facilities available,
- (g) the field staff available,
- (h) the ultimate use of the data obtained.

In some circumstances, sufficient information may be available to formulate a full scale programme at this stage. Nevertheless, provision must be made for any modifications found necessary in the light of incoming data. More usually, some preliminary studies will be required to determine the minimum number of samples, the frequency and time of sampling, and the sampling sites necessary to obtain an adequate description of the conditions of interest in the water body.

Checks of compliance with effluent quality and quantity requirements can best be achieved by determining the flow rates and strengths of the effluent itself at various times. However, this may not always be possible.

In the case of a reported observation of deterioration in water quality, an experience and qualified observer should carry out an on-site evaluation, and advise on further action accordingly.

Several approaches are useful in preliminary studies for programmes to monitor water quality changes or study effluent dispersal and its effects on water quality. Mapping of effluent patterns from any outfall is usually necessary. Efficient methods include :

- (a) horizontal effluent mapping by addition of dye to the effluent. The resulting dye pattern may best be recorded photographically. Polaroid cameras are particularly useful for this purpose,
- (b) vertical effluent mapping by addition of salt to the effluent and measurement of conductivity at known depths at points selected from the horizontal effluent map.

Great care is needed to develop a final programme which is both economical and adequate from the results of the preliminary survey.

The preliminary survey is thus used to establish the minimum sampling programme which will generate data representative of the body of water under study. This introduces the concept of the "representative sample", which may be defined for a given time and cross-section of a water body as "a flow-weighted concentration average". Alternatively, this may be expressed as "the ratio or the rate of transport of the particular constituent through the cross-section at a given time to the rate of transport of water through the same cross-section". Clearly, the concentrations in regions of rapid flow will contribute relatively more to the representative concentration than those in sluggish regions.

It is exceedingly difficult to obtain representative data without excessive effort. In each case the acceptable departure from true representation must be decided and the sampling plan established accordingly.

The water in hydro-electrical dam tail-races is very well mixed so that a good approximation to representative data on the water flowing in the river immediately below the dam may be obtained from one sample. Although generally this data will not be representative of the water above the dam, the concentrations of some species including alkali and alkaline earth metals, chlorides and sulphates may be taken as representative of that water. It should be noted, however, that data representative of only a small section of a water body may be of interest.

Representative concentrations will vary with time. It will be necessary to decide whether typical (time averaged) maximum or minimum concentrations for the relevant period are most appropriate. As with selection of the sampling site, a preliminary time-based study may be helpful in establishing the optimum sampling times and frequency.

If the effect of an effluent discharge is to be determined, then sampling times would in most cases be chosen during which there is a maximum concentration of polluting material with the maximum biological effect. Such conditions will usually coincide with high temperatures and low flows.

For routine work it is more important to examine numerous samples by simple tests than occasional samples by a more complicated series of tests.

4. SAMPLING EQUIPMENT

Any sampling equipment must satisfy a number of requirements which are listed below. A sampler must satisfy the first four and could advantageously incorporate the remainder.

Necessary

- (a) easily freed from contamination,
- (b) must not change relevant water characteristics,
- (c) easy and accurate positioning in the field. This can be difficult in deep waters with a moderate or fast flow,
- (d) gives an adequate sample volume.

Desirable

- (a) robust,
- (b) simple to operate,
- (c) easily constructed,
- (d) easily transportable,
- (e) not too heavy.

Suitable samplers for many situations can be selected from the following list. Some of these samplers are illustrated in the appendix :

4.1 *Pumping System* (See Figure 1)

These have the widest general applicability. They may be flushed easily by pumping to Waste prior to collecting the sample. Pumping methods are particularly useful where large sample volumes are required or where samples are to be taken from a lake without disturbing stratification. If samples are to be taken for the determination of dissolved gases, the water must not be pumped in such a way that the pressure applied to it drops significantly below atmospheric pressure, e.g. by cavitation or by sucking up a high water column.

Where sampled water must flow through the pump, peristaltic pumps or centrifugal pumps with plastic (e.g. viton) heads and impellers may be used. Almost any pump may be used if the sample is collected before the water passes through the pump.

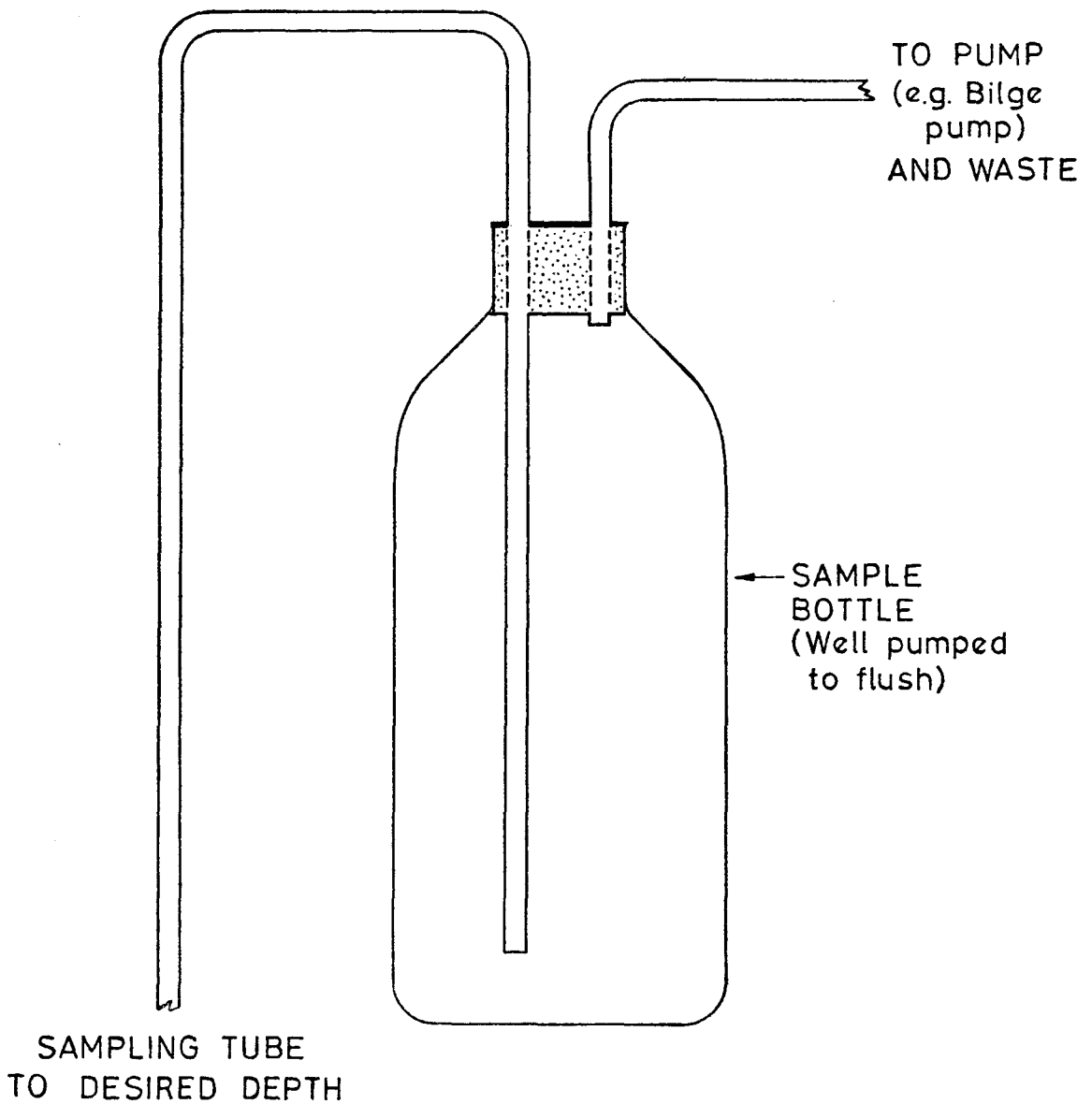


FIGURE 1. SAMPLE COLLECTION USING LOW QUALITY PUMP

In flowing rivers careful consideration must be given to methods for positioning the end of the intake tube accurately.

4.2 *Hand-held Bottle*

Suitable clean sample bottles may be used to collect surface or near-surface samples directly. This is not a satisfactory technique for dissolved gas determinations.

4.3 *Weighted Bottle*

Suitable clean sample bottles may be mounted in a weighted holder attached to a rope and used to collect near-surface samples where the operator cannot conveniently get to the sampling site. In general, a mixture of waters from different depths is obtained by this method. The technique is not satisfactory for dissolved gases.

4.4 *Dussart Sampler* (See Figure 2)

When the sampler has been lowered to the desired depth, the cord is jerked to remove the rubber tube connecting the inlet and outlet so that the air is replaced by water taken from a specific depth. This sampling method is not entirely satisfactory for dissolved gas determination, but may be used in the absence of better equipment.

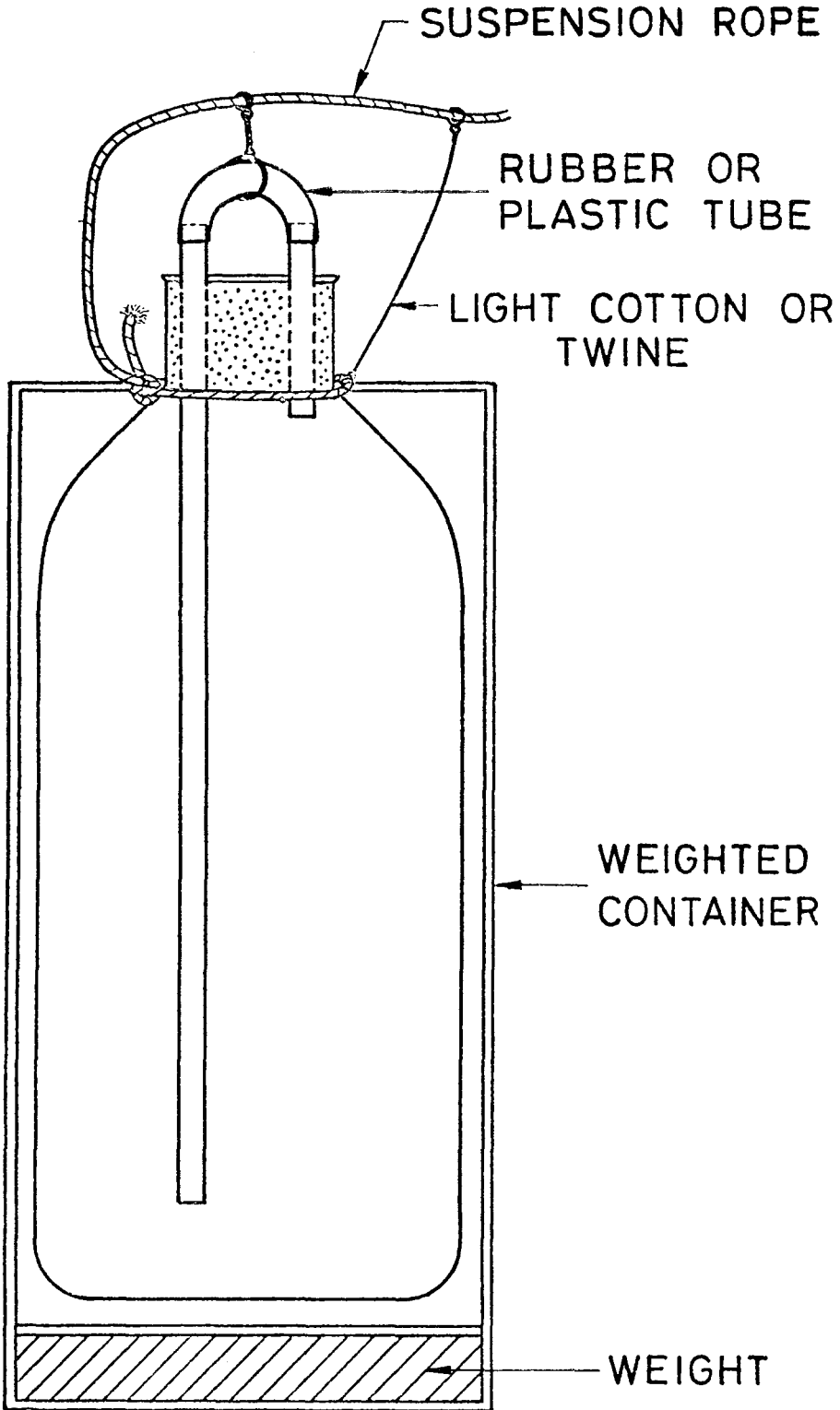


FIGURE 2. THE DUSSART SAMPLER

4.5 Double Bottle Systems (See Figures 3 and 4)

These samplers may be operated at specific depths, as for the Dussart sampler, but in addition the sample bottle is thoroughly flushed, so that the samples are suitable for the estimation of dissolved gases.

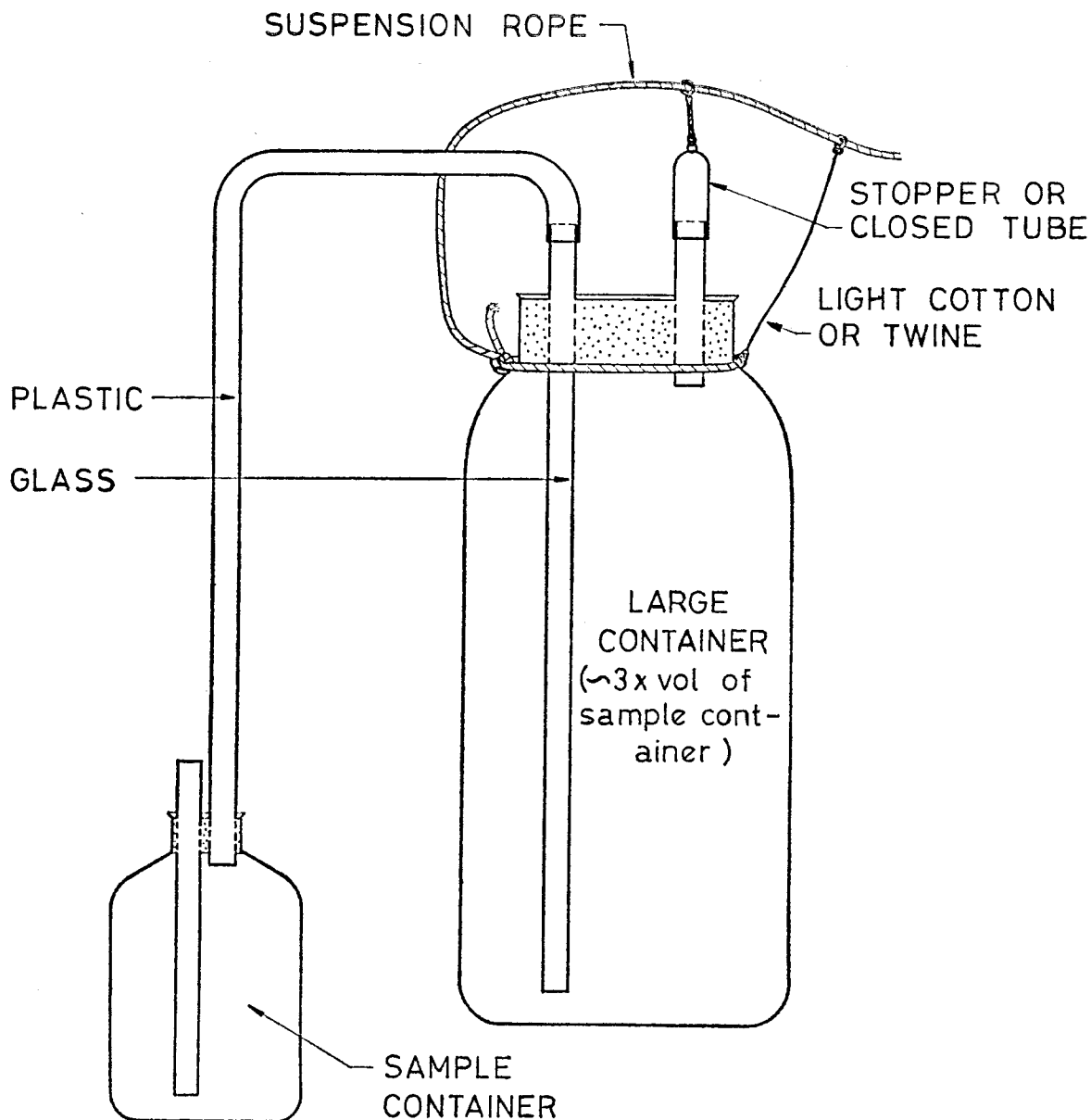


FIGURE 3. DOUBLE BOTTLE SAMPLING SYSTEM
(For Simplicity, Weighting System Omitted)

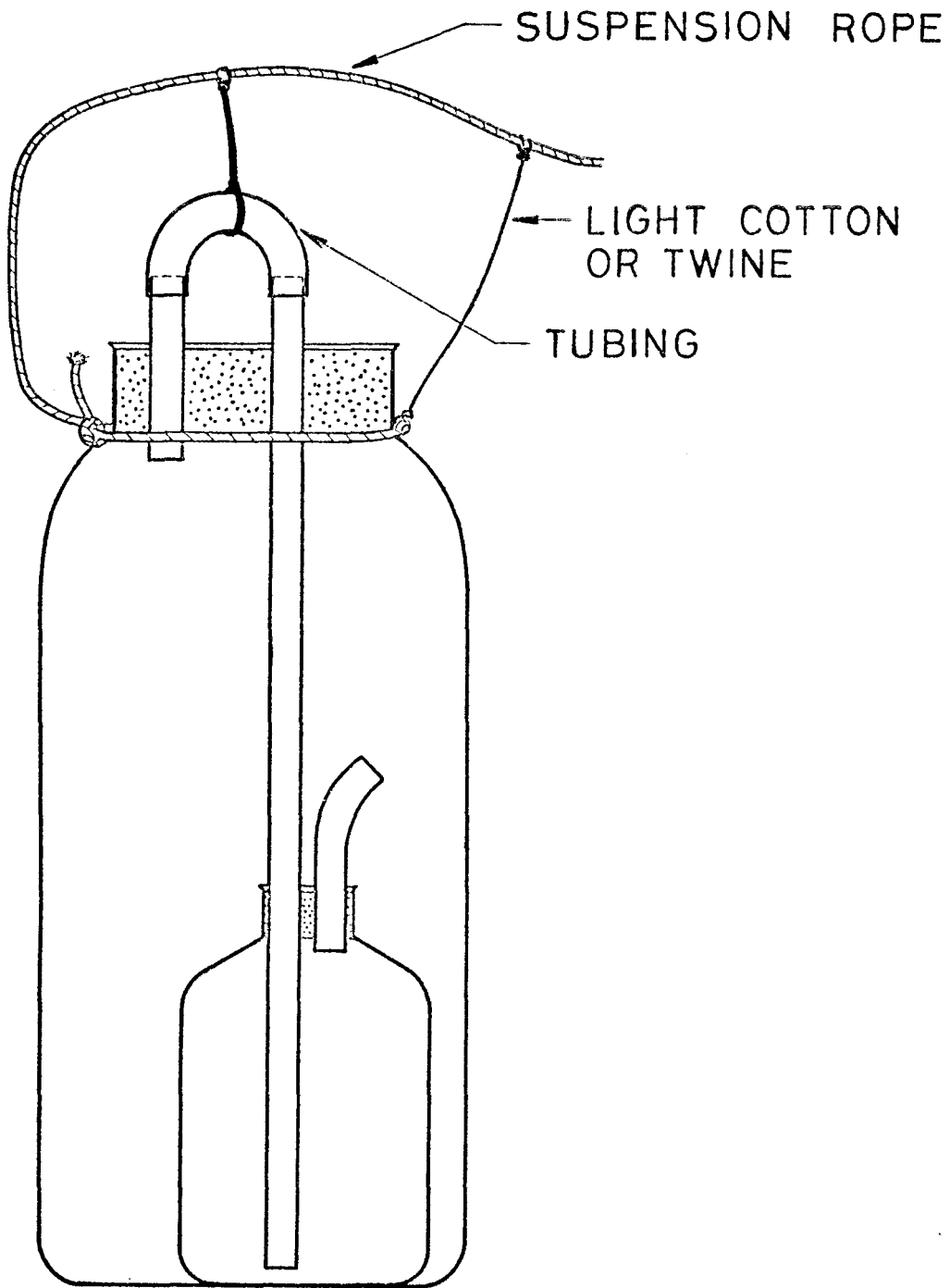


FIGURE 4. DOUBLE BOTTLE SAMPLING SYSTEM
(Weighting Omitted)

4.6 Friedinger Sampler

This sampler has a hinged lid fitted to each end of a tube. As the sampler is lowered to the desired depth, water passes through the tube, thereby flushing it. A system of levers closes the lids at the chosen sample depth.

This device is more difficult to construct, but is suitable for taking samples from a specific depth for dissolved gases and other constituents.

4.7 Modified J-Z Sampler (See Figure 5)

This sampler is particularly suitable for collection of bacteriological samples. The bottle is sterilised in an autoclave and the sealing tubes fitted while hot. When the tube is broken underwater at any chosen depth, the partial vacuum draws a sample into the sterilised bottle.

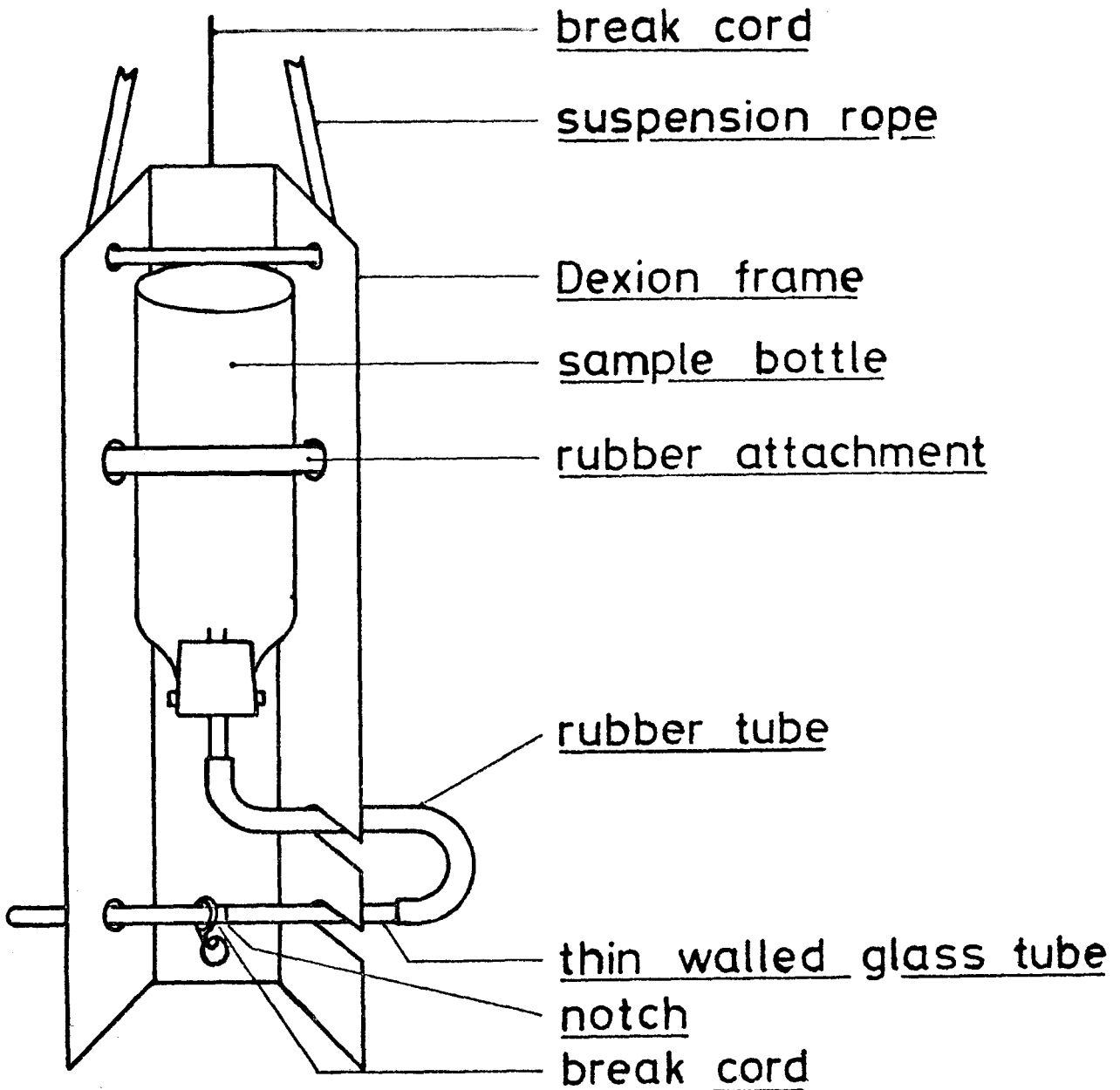


FIGURE 5. MODIFIED J-Z SAMPLER

5. SAMPLE CONTAINERS

- (a) Sample containers for chemical samples should be constructed of polyethylene, polypropylene or of borosilicate ("Pyrex") glass, depending on the species under analysis. Before use, all new bottles must be thoroughly cleaned, filled with water, and allowed to soak several days. Finally they should be rinsed *thoroughly* with distilled water.
- (b) Glass bottles provided with a ground-glass stopper or a metal screw-cap should be used for bacteriological samples. Before use all bottles should be treated as described in Section 7.2 and then sterilised. At least the stopper and neck of the bottle should be protected by a paper or parchment cover, or by a thin aluminium foil.
- (c) Glass bottles for phosphorus samples must not be washed with detergents and must either be rinsed with hot 2N hydrochloric acid or stood overnight filled with concentrated sulphuric/nitric acid mixture, as a part of the cleansing procedure.
- (d) Bottles for samples requiring acidification should be acid-rinsed. Bottles for BOD samples should be filled with chomic acid mixture and allowed to stand for 24 hours prior to thorough rinsing.

6. OPERATION OF SAMPLING EQUIPMENT

6.1 General

Where several samples are being collected on the same occasion from the same source, the sample for bacteriological examination should be collected first, to avoid the danger of contamination of the sampling point during the collection of other samples.

Polyethylene bottles should be filled completely and capped tightly. Glass bottles should normally have a 2 cm air space in the neck, to allow for expansion.

Where a series of samples at different depths are to be taken from the same spot, samples should be taken in order of increasing depth, so that any stratification is not disturbed.

Where the sample bottle is filled directly in the sampling apparatus, the bottle must be decontaminated by the procedures set out in the storage and preservation section, and provision must be made to flush any contamination from earlier samples out of other parts of the system, so that they are not incorporated in the new sample. Where water is transferred from the sampler to the sample bottle, any contamination from previous sampling sites must be flushed out of the sampler before collecting samples. When samples are taken near the bottom, any disturbance of bottom sediments must be avoided.

When sampling for dissolved gases, use should be made of equipment which collects a sample that has displaced water, rather than air, from the sample bottle. Special equipment is needed to collect very deep samples (say over 100 feet) for dissolved gases, because of the possibility of supersaturation of such samples when the pressure on them is reduced.

No simple technique is available for obtaining a representative sample of surface oil and grease, but sub-surface samples can be obtained with a modified Dussart sampler (Figure 2) in which the shorter bottle. Alternatively, a hand-held glass bottle which is half-filled with water can be unstopped underwater. The sample bottle should previously have been rinsed with grease-free solvent and air dried.

Each sample bottle should have attached to it an identifying label or tag. This should specify the water body, sampling site, time of sampling and sample treatment. The following information should be recorded on an additional sheet.

Map reference.

The name of the water body.

The location of the sampling site. This description should be full enough to allow another person to find the exact location without further guidance.

The point of collection, i.e., the position in the cross-section.

The data and time.

The gauge height.

The water and air temperatures.

The type of the sampler.

The collector.

Sample treatment.

General remarks. These should include observations of the weather or any other conditions which might assist in interpreting the analytical results.

6.2 The Hand-held Bottle

This device is perhaps the most widely used of all sampling equipment, and therefore warrants special mention.

When collecting samples for bacteriological or chemical analysis, the sampling bottle should be kept unopened until the moment at which it is required for filling. During sampling the stopper and neck of the bottle should not be allowed to touch anything and the bottle should be held near its bottom. The bottle should be filled, without rinsing, and the stopper should be replaced immediately. Samples can be taken by plunging the bottle, neck downwards, below the surface. The bottle should then be turned until the neck points slightly upwards, the mouth being directed towards the current. If no current exists, a current should be artificially created by pushing the bottle horizontally forward in a direction away from the hand. If it is not possible to collect samples in this way, a weight may be attached to the bottle which can then be lowered into the water. It is important that damage to the bank is avoided, otherwise fouling of the water may occur. Special apparatus is required to collect samples from depth, e.g., the modified J-Z sampler (See Figure 5).

When collecting samples for the analysis of dissolved gases, the water should enter the bottle by a tube extending to the bottom of the bottle, and it should be allowed to overflow by an amount equal to at least three times the volume of the bottle.

7. PRESERVATION AND STORAGE OF SAMPLES

7.1 Introduction

It is desirable to minimise the delay between the taking of samples and their analysis. However the following analyses should be made at the sampling site :

- (a) temperature ($^{\circ}\text{C}$).
- (b) pH—readings are unreliable in soft, unbuffered waters.
- (c) dissolved oxygen—if on-site analysis is impossible:
 - (i) clear sample: Carry the Alsterberg azide procedure through to the liberation of iodine. Chill the sample and store in the dark.
 - (ii) Turbid sample: Collect 500 ml. with the usual precautions, add 10% alum solution (10 ml.) and concentrated ammonia solution (2 ml.), stopper and mix by inversion. Allow the floc and suspended matter to settle and then decant the supernatant into a BOD bottle. Procedure as in 7.1 (C) (i). Note that the Alsterberg method is effected by chemical reducing agents such as sulphate, sulphide or nitrite.
- (d) conductivity,
- (e) acidity (as CO_2),
- (f) carbonate alkalinity—only necessary if pH is above 8.5,
- (g) nitrite,
- (h) turbidity (Secchi disc),
- (i) colour.

7.2 Choice of Preservation and Storage Treatment

In the following tabulation, P refers to polyethylene or polypropylene containers, and G to borosilicate glass containers. The treatments given do not exclude alternative treatments of proved efficiency and should be regarded as tentative.

(a) UNFILTERED SAMPLES

TREATMENT	CONTAINER	ESTIMATIONS
(1) Well mixed, chilled kept in dark	G	BOD, suspended, total and volatile solids; turbidity (if measured within 24 hr); bacteria (special sample).
(2) Well mixed, acidified with conc. sulphuric acid to pH 2.0	G, P	Chemical oxygen demand (COD), nitrite.
(3) Well mixed, mercuric chloride added (1 g/l), kept in dark	G	Turbidity.
(4) Well mixed, mercuric chloride added (60 mg/l), chilled, kept in dark	G	NH_3 , Kjeldahl nitrogen total phosphorus, nitrite, nitrite (after laboratory filtration), chemical oxygen demand (COD).

TREATMENT	CONTAINER	ESTIMATIONS
(5) Well mixed, basified with sodium hydroxide to pH 11.0 or above	G, P	CN.
(6) Settled, supernatant collected, kept cool and out of bright sunlight (minimise aeration)	G, P	Acidity (CO ₂), alkalinity, colour, pH (lab.).
(7) Well mixed (avoid aeration), neutralised (if acid), added zinc acetate (2 g/l)	G	Total Sulphide.

(b) FILTERED SAMPLES

Immediately after collection, the sample should be pressure filtered through a 0.45 micrometer membrane filter, using nitrogen or compressed air. If estimations of phosphorus species are to be made on the filtrate, the membranes should be washed with 2N hydrochloric acid, rinsed thoroughly with distilled water and dried before use.

TREATMENT AFTER FILTRATION	CONTAINER	ESTIMATIONS
(1) None	P	B, Cl, hardness, F, Li, K, Se, SiO ₂ , Na, total dissolved solids, SO ₄ **
(2) Mercuric chloride added (60 mg/l), chilled, kept in dark	G	Nitrate, nitrite, reactive dissolved phosphorus.
(3) Acidified to pH of less than 3.0 with BDH "ARISTAR" nitric acid or its equivalent	P, G	Al, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Ag, Na, Sr, V, Zn.

(c) ALTERNATIVE SAMPLES

While major constituents are not likely to be affected significantly if a sample is laboratory filtered rather than field filtered, there may be marked changes in the levels of minor elements. The following alternative samples treatment can be used, but with reduced confidence in the reported data.

TREATMENT	CONTAINER	ESTIMATIONS
Pressure filtered in the laboratory through a 0.45 micrometer membrane	P	B, Ca, Cl, F, hardness Li, Mg, K, SiO ₂ , Na, total dissolved solids, SO ₄ .

8. RECOMMENDED REFERENCES

- (1) American Public Health Association (1971): Standard Methods for the Examination of Water and Wastewater: 13th ed., New York.
- (2) Golterman, H. L. (1969): Methods for Chemical Analysis of Fresh Waters: *International Biological Programme Handbook No. 8*, Oxford, Blackwell.
- (3) Rainwater, F. H. & Thatcher, L. L. (1960). Methods for Collection and Analysis of Water Samples: *U.S. Geol. Survey Water Supply Paper 1454*, Washington.
- (4) Strickland, J. D. H. & Parson, T. R. (1965): A Manual of Seawater Analysis: *Bull. No. 125, Fish Res. Board (Canada)*, 2nd Rev. ed., Ottawa.
- (5) World Health Organisation (1970). European Standards for Drinking Water: 2nd ed., Geneva.

* In heavily polluted waters, reduce the pH below 8.0 (if sulphite is present), and chill the sample to inhibit bacterial reduction.

PROCEDURE PREVIOUSLY PUBLISHED

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