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THE SAMPLING AND MONITORING OF GROUNDWATER QUALITY

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PREFACE

This report on the sampling and monitoring of groundwater quality was commissioned from the Hydrogeology Research Group of the British Geological Survey by the Department of the Environment. The manual has been prepared specifically for use within the British water industry and an attempt has been made to accommodate the changing needs of that industry following the formation of the National Rivers Authority and the privatisation of the water undertakings.

The report aims to promote scientifically valid sampling and monitoring strategies and offers the basis of a standardised procedure throughout the industry. The compilers are aware that groundwater monitoring is a rapidly advancing technology and hope that periodic revision of the text will be carried out in order to advertise new techniques which may become available in the future.

The development of a national monitoring network in Britain will provide a unique opportunity to test the procedures described in this manual. It also provides the ideal opportunity to drill a limited number of borehole clusters in which each separate borehole will monitor a single horizon or depth at that location without the risk of cross-contamination from other horizons. These cluster sites will provide control to the existing bulk samples which are drawn from numerous production boreholes for which time-series data-sets are already available.

The report was compiled by I.N. Gale and N.S. Robins who are grateful for the contributions made by discussion and of subsequent editing, of many members of both the Hydrogeology Research Group and the Fluid Processes Research Group of the British Geological Survey and of the water industry. The work was compiled under the general direction of the Chief Hydrogeologist, Dr S.S.D. Foster.
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SUMMARY

Accurate sampling and monitoring of groundwater quality is required for many purposes ranging from surveillance of potable water supplies to investigating the nature and extent of aquifer pollution. Groundwater sampling can be a time-consuming and expensive exercise, so care must be taken in the design of a sampling strategy to ensure that the optimum number of samples are collected in order to meet the objectives of the exercise.

A good knowledge of the hydrogeology and local groundwater flow regime is important when planning a sampling programme in order to enable the sensible interpretation of resultant analyses. Preferably, samples should be collected from dedicated monitoring boreholes which are only open to limited vertical sections of the aquifer. Results from these boreholes enable quality changes with depth to be investigated whereas a borehole penetrating the full thickness of the aquifer will only give an integrated sample.

The application of quality assurance programmes is recommended for all aspects of sampling and monitoring of groundwater quality. These programmes should be designed to be as comprehensive and to ensure well-documented lines of decisions, sampling protocols and quality control of sampling methods and analysis.

Techniques for collecting samples from both the saturated and unsaturated aquifers are many and varied. The techniques selected are controlled by the sampling point and the nature of the sample required. In the saturated zone samples of water are either pumped to the surface or collected from a standing column of water using a "grab device". Both these methods have their advantages and limitations which have resulted in the development of numerous specialized sampling devices that are designed to give greater control on what is being collected. These improved sampling methods range from the construction of dedicated sampling boreholes through a whole range of pumping devices to pore-water extraction and packer sampling. In the unsaturated zone, water is sampled using tensiometer and pore-water extraction techniques.

Sampling for different determinants requires specialized procedures to ensure the resultant analysis is representative of the in-situ values. As soon as a sample is collected it is subjected to physical and chemical changes which should be minimised. Some determinands are stable and require little treatment other than filtration of the sample whereas others need to be analysed on site on a flowing sample. The major and minor ions fall into the former category and redox and dissolved oxygen fall into the latter. Most samples need to be preserved by the addition of acid to ensure metals are kept in solution and care should be taken in selecting containers and storage methods that will not alter the nature of the sample. Specialized sampling methods are required for low-solubility determinands, volatile organic determinands, dissolved gases and microbiological populations occurring naturally or as the result of pollution. Sampling of the gaseous and solid phases of aquifers is also discussed as is the latest sampling technology currently under development.
INTRODUCTION

Groundwater quality measurement typically requires the use of a sampling device to produce a sample, the collection and storage and subsequent analysis of the sample for selected determinands. Within this procedure sampling can be the single largest source of error. Modern analytical techniques therefore, demand properly planned and well executed sampling programmes in order to obtain samples which represent specific groundwater flow paths that accurately reflect the quality of the groundwater under investigation (Miles and Cook, 1981). Sampling may relate to a study of ambient groundwater quality, or to a dynamic pollution problem caused by a diffuse or a local source.

Groundwater may be analysed for a wide variety of reasons:

- To determine the suitability of groundwater as a source of drinking water.
- To determine the suitability of groundwater as a source for non-potable uses.
- To identify and monitor the movement of a pollutant caused by potentially hazardous surface and sub-surface activities, such as landfill sites, industry, including extractive industries, and agriculture.
- To monitor groundwater pollution in the vicinity of sources of groundwater used for potable, or other supply purposes, in order to protect the integrity of these supplies and maintain their continued use.
- To develop an understanding of regional groundwater quality variations as an aid to understanding the groundwater regime and to achieve optimal groundwater resource management.
- To assess the impact of changes in land-use on groundwater quality.
- To calibrate and validate groundwater quality models developed for pollution control and resource management.
- To determine flow paths and rates of groundwater movement using injected tracers.

The evaluation of the inorganic and organic constituents of groundwaters provide a valuable tool with which to solve hydrogeological problems. The hydrogeologist, however, must previously have determined as much as possible about the prevailing groundwater regimes using classical hydrogeological techniques before optimum sampling locations can be selected and the appropriate method and procedure of sampling devised.

The techniques available for groundwater sampling in both the saturated and unsaturated zone are many and varied. This manual aims to describe those techniques and their advantages and disadvantages. The manual will assist in selecting the optimum equipment and procedure for the prevailing conditions and the required determinands. References to major or informative works are cited and include a selection of previously published guides to groundwater sampling as well as papers describing particular techniques and innovative procedures. There are numerous other articles in the literature relating to specialised equipment or techniques, most notably in the American journals, Ground Water Monitoring Review and Ground Water.
The manual has been compiled by the British Geological Survey Hydrogeology Research Group on behalf of the Department of the Environment. Consultation with the Water Industry in the United Kingdom indicated an awareness of the need for good groundwater sampling and generally an awareness of the current inadequacies in the sampling methods and monitoring strategies. It is hoped that this manual will draw attention to preferred procedures and promote greater efficiency and quality control over groundwater sampling in the future.
1. MONITORING STRATEGY

1.1 DESIGN OF MONITORING PROGRAMMES

Routine monitoring of groundwater quality is most often carried out to determine deterioration with time. These data are expensive to collect, particularly if boreholes have to be drilled specially for monitoring, so care must be taken to ensure the data are useful and representative of the aquifer being monitored.

Wilkinson and Edworthy (1981) identified four major reasons why groundwater monitoring systems yield inadequate data:

- the objectives of the monitoring programme are not properly defined.
- the monitoring systems are installed without sufficient hydrogeological knowledge of the area.
- insufficient planning of sample collection, handling, storage and analysis of samples.
- data are poorly archived.

Despite these inadequacies, data are often used for long term predictions of water quality and as the basis for decisions on major capital expenditure. Careful planning of a groundwater monitoring system is therefore vital in order to gather useful, unambiguous data on which sound decisions can be made (Foster and Gomes, 1989). Although apparently expensive, groundwater monitoring systems can be very cost-effective and lead to better aquifer management. This is particularly so now that aquifers are being put under increasing stress from abstraction, waste disposal, mining activities and diffuse and point-source pollution.

"The aim of a groundwater quality monitoring programme is to draw a picture of spatial distribution of each groundwater quality parameter and how that distribution changes in time either naturally or under man's influence." (Wilkinson and Edworthy, 1981).

Planning new groundwater sampling and monitoring programmes, or revision of existing programmes, should preferably be organised to incorporate current quality assurance (QA) practices. QA is becoming an increasingly important factor in all fields of activity and is especially applicable in groundwater monitoring and sampling programmes as the stress on groundwater resources increases due to increased use, more complex management of resources (aquifer recharge, stream augmentation, in-situ groundwater treatment etc.) and pollution of aquifers from both diffuse and point sources.

The US Environmental Protection Agency (EPA) has compiled guidelines and specifications for quality assurance of all aspects of groundwater investigations. These guidelines are discussed by Van Ee and MacMillion (1988) who stress that programmes of quality assurance should be devised prior to a study to ensure collection of scientifically and, if necessary, legally sound data. They also point out that the development of excessively rigorous QA standards may have undesirable effects such as cost increase in excess of benefits.

QA programmes can be as extensive and comprehensive as necessary but care should be taken to design the programme to a level that is practical for the resources available. A quality assurance programme should ensure a well documented and traceable line of decisions and procedures with periodic checks,
1. Title page, with provision for approval signatures
2. Table of contents
3. Project description
4. Project organisation and responsibilities
5. QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability
6. Sampling procedures
7. Sample custody
8. Calibration procedures, references and frequency
9. Analytical procedures
10. Data reduction, validation, and reporting
11. Internal QC checks and frequency
12. QA performance audits, system audits and frequency
13. QA reports to management
14. Preventive maintenance procedures and schedules
15. Specific procedures to be used to routinely assess and document data precision, representativeness, comparability, accuracy and completeness of specific measurement parameters involved
16. Corrective action

TABLE 1. Required elements (when applicable) for QA (project) plans for monitoring and measurement projects (QAMS-002/80)
by someone not directly involved in the project, to ensure standards of quality control, integrity of methods of analysis and accurate interpretation of results. The EPA devised a list of elements of a QA programme (Table 1) applicable to environmental studies in general. This list can be applied in the planning stages of a groundwater sampling and monitoring programme.

Groundwater quality monitoring can have different objectives on national, regional or local levels and these objectives should be clearly defined and documented. The two main areas of interest are surveillance of potable water supplies and monitoring of pollution, either diffuse or point-source.

Groundwater quality is variable, not only spatially in 3-dimensions but also with time. The latter variations can be cyclic on an annual basis or over much shorter periods related to recharge events. Areal variations are usually gradual but the hydraulic characteristics of an aquifer can result in considerable variability with depth, controlled by high permeability layers or fissure-flow zones (Brassington and Walthall, 1985). These variations can occur in an aquifer in its natural state but the system is further complicated by pumping, artificial recharge or pollution.

Prior to embarking on a new groundwater quality monitoring system or reviewing an existing system, the objectives, both short and long-term, must be clearly defined. If the system is to monitor an aquifer regionally, the optimum number and distribution of sampling points must be determined, to ensure that sufficient good quality data are collected to meet the objectives. Similarly, if a local source of pollution is to be monitored then the selection of sampling points both areally and with depth is vital.

The optimum number of monitoring wells and the frequency with which they are sampled can be evaluated statistically (Ward et al., 1979; Bachmat and Ben-Zvi, 1981). The latter paper investigates the relationship between the number of sampling points, their spatial configuration and the sampling frequency in order to derive an optimal sampling programme.

Monitoring existing water supply boreholes will provide data on changes in water quality that have occurred but will not give warning of a pollutant moving towards the borehole. Additionally, pumping boreholes provide a bulk sample for the thickness of aquifer penetrated and do not give an indication of water quality from different production zones.

Once the objectives of any groundwater quality monitoring programme have been clearly defined the next essential step is to obtain as full as possible an understanding of the hydrogeological regime of the region or area of interest. This can usually be obtained from existing data or by comparison with a similar area, but may involve an investigative programme of logging existing boreholes or even drilling. Without knowledge of the groundwater flow regime, groundwater quality monitoring can be either misleading or financially wasteful due to monitoring in the wrong place or at the wrong depth.

On a site-specific scale, a knowledge of the well design and hydraulics is vital so that the origin of the water sample is known. For example, a borehole may penetrate two aquifers where, because of different piezometric heads, water from the first is flowing into the second. A depth sample will only give the water quality of the first aquifer. Only by isolating the second aquifer using a packer system or other suitable device, can a representative sample be obtained.
Similarly, the location of monitoring boreholes must be selected with due regard to the regional and local groundwater flow regime. For example, if a water-supply well shows signs of pollution then the regional groundwater flow regime, modified by local pumping, will indicate the most likely source of the contamination. The nature and extent of the pollution plume can then be investigated using the minimum number of boreholes.

Boreholes that are specifically designed for monitoring offer several advantages over non-dedicated boreholes. The single-screen borehole allows head measurements and samples to be drawn from a single horizon. Clusters of single screen boreholes provide information from different horizons at the same location. The extra cost of installing and monitoring clusters is justified by the increased value of the data so obtained. These data include information on differential head with depth, and variations in water quality from one horizon to the next.

Long-screen boreholes only provide a general picture, short single-screen boreholes offer the essential details. Reconnaissance work has to be carried out using existing boreholes. The preliminary data so obtained must then be used to design a monitoring system with cluster groups placed strategically within each aquifer. It is desirable to maintain some of the original long-screen monitoring boreholes although the data they yield will need to be reviewed with time.

1.2 MONITORING FOR SPECIFIC OBJECTIVES

Once the objectives of a groundwater quality monitoring programme have been identified and documented and the best possible understanding of the hydrogeological regime has been formulated the sampling programme can be designed in detail. The main decisions to be made relate to the number of sampling points, the frequency of sampling and the determinands to be monitored at each sampling point.

A policy of frequently sampling every borehole and other available sample points for a wide range of determinands is obviously not going to be cost-effective and operation of a monitoring system needs to be regarded in two stages (Wilkinson and Edworthy, 1981).

Firstly, a period of initial assessment, usually for a complete year, where frequent sampling of available sources for a wide range of determinands identifies seasonal fluctuations and key determinands which can act as indicators later in the programme. The second stage of the programme entails long-term surveillance when sampling frequency and number of determinands are reduced to optimise costs, but still meet the objectives of the sampling programme. For example, once the general hydrogeochemistry of an area has been defined it may be sufficient to measure chloride levels, quarterly, to monitor saline intrusion.

These criteria can be applied even to existing monitoring programmes which have been in operation for many years. The programmes may require review to reassess the objectives, evaluate the current sampling points for suitability of location and horizon from which water is collected. An assessment of the frequency of sampling and the range of determinands monitored may result in financial savings. Objectives of regional monitoring programmes will change with time in a dynamic groundwater system with changing demands in supply, waste disposal and the water quality deterioration due to pollution.
Poor archiving and accessibility of data was identified by Wilkinson and Edworthy (1981) as one of the main areas of inadequacy in groundwater quality monitoring programmes. From the preceding discussion it is apparent that gathering groundwater quality data is a time-consuming and very expensive process. Often the data gathered on a specific project are not archived effectively and the data are lost or inadequately recorded for future use. Historic data are very valuable when studying temporal changes in water quality.

Handling and storage of data should therefore be included in the original planning of the monitoring and quality assurance programmes. The data archiving system should be designed to be readily accessible to other members of the team working on the current project or monitoring programme, other members of the organisation and other interested parties.

Currently, data storage systems should be computer based to facilitate handling of large volumes of data. These systems should be compatible with data handling packages capable of assimilating and plotting the data to facilitate presentation and compilation of reports.

1.2.1 Potable Water Supply Surveillance

Monitoring water quality from a public supply borehole is primarily to ensure the consumer is provided with a "wholesome" supply that meets the relevant water quality standards. This is achieved by very frequent, or even continuous, monitoring of selected determinands at the source prior to treatment so that rapid action can be taken if one or more determinands should change to an unacceptable level. Only a few indicators such as pH, colour and microbiological determinands are monitored in this way with a more extensive analysis being carried out at a longer interval, say every 3 or 6 months. This latter data set can be used to monitor the long-term changes, provided the sampling interval is suitably selected.

1.2.2 Pollution Monitoring

Pollution of groundwater bodies can be classified into two main groups:

- diffuse pollution where the water quality deteriorates over an area or region. This type of pollution includes the leaching of nitrates and other agrochemicals and the effects of acid rain. Also included in this group are the pollution effects of a large number of point sources, particularly in urban areas, which result in general pollution over a wider area.

- point-source pollution relates to the local pollution caused by waste disposal practices or accidental spillage. Line-source pollution is included in this group and relates to the effects of motorways and railway lines.

The design of water quality sampling regimes to investigate and monitor these different types of pollution using different determinands obviously requires very different approaches.

1.2.2.1 Diffuse Source

Diffuse pollution of groundwater in the UK and Europe has received a great deal of attention in the last two decades because of the concern about nitrate pollution. Nitrate-rich fertiliser, applied to increase productivity
of arable crops and grassland, has been leached to varying degrees through the unsaturated zone to major aquifers, particularly in the unconfined areas of recharge (The Royal Society, 1983; Foster et al. 1986; SCA 1986).

In general, the problem has been defined as pulses of nitrate moving slowly through the unsaturated zone over a period of 10 to 40 years, depending on the thickness and hydraulic characteristics of the rock. Once the nitrate reaches the water table it moves relatively rapidly with the groundwater flow, either on a natural gradient or one modified by pumping. Pesticides are thought to move in a similar manner but their occurrence and movement have not yet been studied in detail.

Monitoring this type of pollution poses special problems. If the problem is approached wholly by surveillance of water quality from supply wells, then when the increase in level of determinand is recorded, the pulse of pollutant has already reached the water table. Any subsequent increase in concentration is then liable to be relatively rapid and levels may quickly exceed the statutory limits. Little time is then available for remedial action and the source may even have to be removed from supply.

Early warning monitoring networks are required in both the saturated and unsaturated zones. In the latter zone the methods described in Section 2.3 can be used to sample a point repeatedly, or water quality profiles can be derived from pore-water extracted from cores. Once a "pulse" of pollutant has been identified in a profile through the unsaturated zone, its movement is best monitored by subsequent sampling at the same site at intervals of 3 to 5 years in a rolling drilling programme.

Regional monitoring of the saturated zone is best achieved in purpose-drilled monitoring boreholes. The purpose of the monitoring programme must be clearly defined and sample point locations and depths identified to ensure representative samples are collected. In an area where diffuse pollution, such as nitrates or pesticides, is thought to be moving vertically towards the water-table then monitoring the zone of fluctuation will identify the initial arrival at the zone of saturation. Similarly, when monitoring the lateral movement of a pollutant, sample depths must be selected in zones of preferential flow.

A system to enable even earlier warning requires the monitoring of the unsaturated zone at sufficient sites to be able to model the likely input of pollutant in an area. Although the pollution is diffuse it is also variable with such factors as rate of application, nature of soil and rock, precipitation, thickness of unsaturated zone, type of crop grown and natural attenuation. All these factors influence the amount of pollutant eventually leached to the groundwater. The design of a monitoring network would therefore require these factors to be taken into account in deciding on the minimum number of sampling sites to achieve the objective of quantifying the future pollution problem.

The selection of determinands to be monitored relates to the type of pollution under investigation. Leached nitrate from whatever source is relatively easy to measure as the levels of interest are of the order of tens of milligrams per litre. The concentrations of the nitrogen species and a selection of major ions can be determined from a few millilitres of sample which can usually be obtained by centrifugation of rock from the unsaturated zone (Section 2.2.3.4).
Much greater difficulty is attached to sampling for pesticides as the recommended limits and the concentrations likely to be encountered are about four orders of magnitude lower than those of nitrate. A much larger volume of water, usually a minimum of two litres, is required for analysis. In addition, a wide range of chemical compounds are employed and could potentially be present, together with their breakdown products. Pesticide analysis is expensive, so a few compounds should be targeted for analysis. Selection should be based on records of pesticide application in the area under investigation, together with an assessment of which compounds are most likely to leach to groundwater, based on their properties of solubility and persistence and their methods of application.

Water for pesticide analysis is best gathered using an in-situ tensiometer which will collect an integrated sample over a period of time. If the nature of the rock precludes the use of tensiometers (e.g. the pore-size in the chalk is too small for tensiometers to be effective) then coring and extraction of pore-water by centrifugation is possible, but expensive and time-consuming, because of the relatively large quantity of rock that requires processing. Currently no wholly satisfactory method for sampling the unsaturated zone for agrochemicals exists. Probably the most effective method of providing early-warning of agrochemical pollution is a network of piezometers that monitor the water-table in the zone of fluctuation at a suitable time interval.

1.2.2.2 Point Source

Point-source pollution of groundwater bodies can originate from a multitude of sources, most commonly landfill sites, from which leachates originate and percolate into the aquifer. The nature of the leachate and its potential to pollute the aquifer depends on the landfill site, its geological setting, the type of waste (domestic or industrial) and the effectiveness of the management.

Slurry dams containing waste from mining or industrial processes are another type of point-source pollution, as are accidental spillages and illegal dumping of oils, fuels and chemicals. Particularly serious problems can arise where natural storm-water drainage from roads, railways or airport runways are designed to flow into underground sumps. This practice can directly recharge an aquifer and, if an accidental spillage occurred at the site of the soakaway, serious pollution of the aquifer could occur.

Pollution associated with major lines of transport is referred to as line-source. Both roads and railways need to be kept free of weeds by application of herbicides, but excess can be leached to underlying aquifers. Other linear structures, such as pipelines, are potential line-sources of pollution but leakages are more likely to be restricted to point-sources along the length.

Each case of point-source pollution is an individual event and although similarities between events will occur the approach made to determine the nature and extent of the pollution requires flexibility. Monitoring of point-source pollution events needs to be tackled in a systematic manner in the following stages:
a) Evaluation of existing data

The location of the site in relation to the geological, hydrological and hydrogeological environment needs to be assessed. The historical record of inputs and operation of the site or nature of the spillage requires investigation in order to form a preliminary model of the likely chemical and physical nature of the pollutant.

An understanding of the transport of the contaminant originating from a point-source is required and this is discussed in detail by Freeze and Cherry (1979). Dispersion processes can be both physical and chemical and the relative importance of these effects will determine the shape of the pollutant plume. Input of the pollutant may be continuous and still active or the source of pollution may have been removed or the input may be cyclic. The resultant pollutant plumes will vary greatly and may be found a considerable distance down-gradient with no sign of contamination adjacent to the site. The density of the pollutant plume can also affect its shape and demands careful selection of the depth of sampling points. Inhomogeneities in aquifers, particularly fissured aquifers and complex alluvial aquifers with sand and clay lenses, will further complicate the shape of pollution plumes both areally and with depth.

b) Preliminary monitoring network

The preliminary model is liable to have many unknowns such as detailed local geology, hydraulic properties of the aquifer and groundwater flow-regime. These need to be determined by drilling and testing but the operation should be carried out in conjunction with installation of a network of monitoring-wells to identify the nature and extent of the pollution plume. Because of the expense of drilling and installation of monitoring wells, the selection of sites, both upgradient and downgradient of the point-source, should be carefully made. The three-dimensional nature of the system must be taken into account by completing monitoring wells at different depths.

c) Monitoring network

Utilising the results of the first two stages, the preliminary model is revised and further gaps in the understanding of the system identified. These gaps should be filled by drilling further monitoring wells for inclusion in the monitoring network in conjunction with the design of the sampling strategy. As described in Section 1.1 this will involve an initially intensive programme to identify indicator parameters, which can be monitored at frequent intervals, supplemented by more comprehensive sampling at suitable intervals.

These three basic stages of an investigation should enable the pollution from a point-source to be identified and its nature, extent and rate of movement quantified. This information can then be used as a basis for predictions of detrimental effects likely to be inflicted on the environment and water-supply and assist in the decision as to what remedial action should be taken.

1.2.3 Research Investigations

The three main areas of groundwater quality sampling and monitoring are regional assessment, monitoring the quality of pumped public-supply systems and monitoring pollution. Other specialised investigations dependent on accurate measurement of groundwater quality are also carried out but the principles described in the previous sections apply.
Monitoring the extent and movement of induced saline intrusion requires an understanding of the hydrogeological regime with the additional complication of fluids of differing densities. The use of tracers to determine the direction, path and rate of groundwater movement not only requires accurate sampling but more importantly a knowledge of the hydraulic regime and a good understanding of what is being sampled.

Other areas of research include the study of the effects of deep waste disposal, both solid and liquid, the storage of fluids in aquifers or reservoirs, in-situ groundwater treatment to improve quality and storage of thermal energy in aquifers. These and many other exotic uses of aquifers require the sampling principles described in this manual to be applied to the specific problem as appropriate.
2. SAMPLING TECHNIQUES

2.1 GENERAL SAFETY PRECAUTIONS

Safety at wells, boreholes and drilling sites, in trenches, chambers, mines and other areas is dependent on knowledge of potential hazards as much as common sense. If in doubt - ask. Above all take care and work in pairs (Institution of Civil Engineers 1972).

Physical dangers may arise from collapse around or into old excavations, wells or boreholes due to failure of structural supports and formation wash-outs. Physical dangers are also present at all drilling sites at all times, and instructions from the drilling rig operator must be obeyed promptly. Toe-protection footwear and hard-hats are mandatory on drilling and borehole test sites. Additional protective clothing is desirable particularly if toxic or radioactive groundwaters are to be sampled. In the latter case advice should be taken from qualified health physics personnel before and during sampling.

A particular hazard can arise from the occurrence of gas which can collect in wells, well-head sumps and enclosed basements. This is commonly a gas that is deficient in oxygen and consists of nitrogen mixed with carbon dioxide. Other gases encountered underground are carbon dioxide, methane and hydrogen sulphide; the latter two are explosive. Carbon dioxide is a component of foul air but it is also found in most rocks, particularly limestones, or where acids have been used, for example to improve permeability. If the atmospheric pressure falls, a well may begin to discharge carbon dioxide (or foul air) and this can collect at a well-head or in sumps if ventilation is poor. Thus, gas can begin to collect in an area that has previously been tested and found to be free of gas.

Carbon monoxide and petrol and diesel vapours can collect in wells, sumps and basements when internal combustion engines are operated nearby. Fumes can accumulate from spills of petrol and diesel.

Hydrogen sulphide has a characteristic smell of rotten eggs but the sense of smell rapidly declines in the presence of this gas; very small amounts cause death quickly.

Methane is associated with carbonaceous strata and landfill sites. It is lighter than air and, therefore, accumulates near the roofs of closed chambers or adits. High concentrations lead to suffocation. It is explosive at low concentrations. Wells, well-head sumps, basements that contain a well or borehole, and sampling or inspection pits must never be entered without first testing for gas. Tests must be continuously carried out while working in such environments. This must include tests below the working level. The tests must be made with authorised flame safety lamps or gas detecting apparatus. A naked light must never be used if explosive gases such as methane are suspected. The detector should not be lowered on a nylon line because of a risk of generating static electricity in an explosive atmosphere.

Where there may be highly volatile hydrocarbons any operations of drilling or sampling must be carried out in a safe manner. All machinery must be fitted with flame traps and spark arresters, and there should be no arcing to the atmosphere from any switchgear. Hydrocarbon detectors and alarms should be used, and the need for having adequate fire fighting equipment available should be surveyed.
If it is necessary to enter a well, it must only be done when at least two other people are present. A proper safety harness must be worn connected to a lifting system or mechanism by which an individual can be recovered if he/she becomes unconscious. Never enter a well with a make-shift harness such as a rope around your waist. One person, or even two, cannot lift an unconscious person by such a means. Hanging from a rope for even a short time can be dangerous or even fatal.

2.2 SATURATED ZONE SAMPLING

The saturated zone of an aquifer is that part where all interconnected pore spaces, fractures and other voids contain groundwater at a pressure equal to, or greater than, atmospheric pressure. The groundwater can move freely within the rock in the direction of the prevailing hydraulic gradient. In an unconfined aquifer the upper surface of the saturated zone is the water table, at which surfacethe pressure of the groundwater is equal to that of the atmosphere. Where an aquifer lies beneath an impermeable (or confining) layer such as a clay, the aquifer is confined and the water pressure at this boundary is termed the confining or piezometric head; the head is described by the potentiometric surface or the level to which water will rise in a borehole penetrating the confining layer.

2.2.1 Sources of Problems

Natural groundwater chemistry is the result of interactions between water and the soil and rock through which the water has passed and in which the water is contained. Groundwater derives largely from meteoric water infiltrating the ground and passing vertically through the unsaturated zone to the saturated zone of the aquifer. There may also be some connate water present. Infiltrating water attains a horizontal flow component only when it arrives at the saturated zone. Full chemical equilibrium between water and rock only occurs in slow-moving groundwaters.

Recharging water may contain pollutants derived from near surface, domestic, industrial and agricultural sources which may be regional or local in nature. A pollutant may be highly soluble, or relatively immiscible, lighter or heavier than water and will behave in the saturated zone according to its physical and chemical characteristics. This behaviour may encourage concentration layering which can be further accentuated by differential flow rates associated with vertical inhomogeneity of aquifers, such as coarser grained, more permeable, layers or open fractures.

In an unconfined aquifer, recharging waters tend to remain at shallow depths and older and more mineralised waters tend to occur at greater depth. This trend continues as groundwater flows into the confined part of an aquifer, accompanied by characteristic changes associated with the decreasing availability of oxygen away from the recharge zone (Edmunds et al., 1984).

Vertical mixing of groundwaters occurs with time and provides additional problems in groundwater sampling and interpretation. Layered sequences of permeable and impermeable strata may create a series of semi-confined aquifers, one above the other, each with a different piezometric head. This gives rise to vertical flux and the potential for upward or downward flow with consequent mixing wherever the confining layers are relatively permeable.

Where concentration layering occurs, production boreholes withdraw a "cocktail" of groundwater according to the relative transmissivity of each layer, the pumping rate, the design of the borehole, the depth to the pump...
intake and the period of pumping. This cocktail results from the mixing of groundwaters from different depths and the mix will vary with pumping period and pumping rate (Wilson and Rouse, 1983). Pumping a borehole in an unlayered aquifer draws water from further afield as pumping proceeds and this too can result in changes in water quality.

Additional problems derive from the borehole construction. In general, percussion and air-hammer drilling techniques provide a cleaner borehole than rotary methods, but in all cases comprehensive well-development and purging is essential before collecting samples.

2.2.2 Limitation of Common Sampling Methods

Groundwater is commonly obtained from boreholes and wells as pumped samples or grab samples. Pumped samples are taken from as near to the wellhead as possible; wellhead sampling taps are often provided for this purpose. These samples are drawn from the aquifer penetrated by the borehole and represent a mixture of undefined proportions which may vary with pumping rate, pumping depth and period.

Depth samples are obtained by lowering a grab device into a borehole to a selected depth where the sample is trapped and withdrawn. This allows vertical variations in water quality to be measured, but samples may suffer contamination from well construction materials or cross-contamination due to vertical flow in the borehole from one horizon to another. A range of grab samplers is available for collecting waters from unpumped wells and boreholes and these are discussed more fully in Section 2.2.2.2.

There is often a need to purge stagnant water in the borehole before sampling. However, there may be a conflicting need to monitor standing water columns as certain determinands require that the natural environment of the groundwater be retained as much as possible so that degassing and loss of volatile substances are restricted. To this end, special techniques have been devised but they are all restricted in scope and applicability.

2.2.2.1 Production Borehole Samples

Pumped borehole samples derive from mixed and ill-defined origins. However, long term pumping provides valuable bulk samples of groundwater from production boreholes (Clark and Baxter, 1989). Permeability stratification in an aquifer promotes abstraction from higher transmissivity layers. However, fissure flow along joints, bedding planes or other discontinuities allows less permeable horizons to drain slowly over a wide area into fissures which can flow rapidly to the borehole. Differential piezometric pressures within strata penetrated by the borehole may also favour abstraction from selective horizons and the location of the pump inlet will prejudice the near field rather than the vertically more distant levels.

The pumping rate and the time since pumping began will also influence the producing zones of an aquifer system. As pumping commences the water standing in the borehole adjacent to the pump inlet is drawn first, then water in the aquifer near the borehole will begin to move forward, and, with time, water from further afield will arrive at the pump inlet. In a layered aquifers, the relative dynamic stress on each permeable horizon will change with time and the volumetric ratio of the water derived from each source horizon will vary. In an unconfined aquifer, dewatering will commence around the borehole and as the cone of depression expands a greater proportion of the water will be drawn from further afield and from deeper in the aquifer.
Borehole construction and design will greatly influence the hydraulic regime around a production borehole. Adequate hydraulic continuity must be available between borehole and aquifer or borehole and intended sampling zone; only if the borehole design is properly recorded can the sampling regime be adequately described. The risk of cross-flow from other permeable horizons, which are not intended to be sampled, is commonly considerable.

In summary, the zone sampled in a production borehole, and hence the ultimate analysis of the sample, depends on the following factors:

i) groundwater regime,
ii) depth to pump inlet,
iii) pumping rate
iv) time since pumping started
v) borehole design.

It is, therefore, essential that the local hydrogeology, groundwater flow patterns and construction of the borehole to be sampled are reasonably well understood before undertaking any detailed hydrochemical investigations based on pumped samples.

Care must be taken with the interpretation of analyses derived from pumped samples. Anomalous data, possibly caused by the factors listed above, should be identified in order to separate short-term effects from long-term trends. A standardised sampling procedure is desirable in order to ensure that the sample mix derived from the aquifer system is reasonably consistent.

Mixed samples drawn from a pumped borehole may be of value on a regional scale (Clark and Baxter, 1989) but are often insufficient for the investigation of groundwater pollution (Parker and others, 1983). Samples will not provide information regarding the progress of a pollution plume, as this may be concentrated in one small horizon or along one bedding plane or joint, and dilution with unpolluted water from other horizons may render the pollutant undetectable. The zones of adverse quality cannot be identified from this type of sample.

Pumped samples are liable to contamination by the very process of pumping from a borehole and discharging at surface. An air-lift pump is least desirable as it produces a water and air mix which destroys the stability of the sample. Submersible and turbine pumps, although better, effect a pressure release at surface which encourages out-gassing from the sample and possible uptake of oxygen from the atmosphere. The turbulent effect of the pump may increase the water temperature by up to 10°C and this in turn may affect the stability of the sample.

2.2.2.2 Grab Sampling in Unpumped Boreholes

A variety of depth sampling devices are available to suit different conditions and requirements (Sinton, 1986). The traditional depth sampler is the grab sampler, which may comprise a simple bailer or some triggered valve device designed to entrap a sample at a given depth in a borehole (Figure 1). Improved equipment such as gas-drive samplers, bladder pumps and peristaltic pumps, which may be used in conjunction with packer systems to isolate selected borehole zones, are described in Section 2.2.3.

The depth sampler enables a small volume of borehole water to be lifted to the surface. However, it offers very little control because the sample is
FIGURE 1. Some tubular groundwater sampling bailers (after Sinton, 1986).
derived from the borehole column and not the aquifer and the volumes removed are too small to have any purging effect on the borehole. The borehole column may be stagnant or it may be flowing over certain interconnected sections of aquifer under differential head, and the depth sample may not represent groundwater from the depth at which it is acquired. In the case of a stagnant water column, interaction between the borehole casing and the atmosphere, and the presence of bacteria which may act as a catalyst to ion exchange, may produce a water which bears little resemblance to the true groundwater (Marsh and Lloyd, 1980).

2.2.3 Improved Sampling Methods

Improved sampling techniques are required to provide more meaningful data, but sophisticated sampling techniques require increased resources. Some techniques require purpose-built monitoring boreholes; the benefit of the data so acquired must be balanced against the increased cost of acquiring it.

2.2.3.1 Purpose-Designed Boreholes

Narrow monitoring boreholes of nominal 50-100 mm diameter are widely used for pollution studies. However, cleaning such boreholes may be difficult and special sampling and pumping equipment is required. Monitoring boreholes should ideally be not less than 100 mm completed diameter and may alternatively be completed to 150 mm or 200 mm nominal diameter. This ensures that proper cleaning and completion of the new monitoring borehole can be undertaken. The casing and borehole screen should be manufactured from material that will not react with the determinands to be sampled. Materials commonly in use are PVC, ABS, polypropylene, teflon, mild and stainless steel, and their advantages and disadvantages are listed in Table 2.

The use of drilling fluids should be reduced to a sensible minimum and preference should be given to air or water circulation (Keely and Hoateng, 1987). Water may have to be introduced during cable-tool percussion drilling; water or air will be necessary for rotary drilling; and air for down-hole hammer percussion. The use of drilling muds for rotary drilling is not recommended for the construction of monitoring boreholes and salt-weighted muds should not be used under any circumstances. Bentonite, for example, may chemically interfere with the groundwater and adsorb certain ions and exchange others; biodegradable polymers tend to leave an organic residue and affect microbiology; and the use of cement in borehole completions may increase the pH of groundwater. A full record should be maintained of all fluids used during drilling and completion. Alternative drilling techniques which enable core samples to be collected are described in Section 2.2.3.4. The advantages and disadvantages of each drilling method are summarized in Table 3.

Cleansing of drilling equipment and completion materials is recommended before use in monitoring boreholes, and is best undertaken by steam cleaning. Decontamination solutions include sodium bicarbonate (water softener), trisodium phosphate (detergent) and calcium hypochlorite (disinfectant).

Borehole development and cleaning are essential. Walker (1983) showed that drilling fluid additives could be detected in one borehole two years after drilling was finished. The effects of bentonite on water samples and of organic residues from polymeric muds decline with time, but they may remain detectable for the first 90 days and may interfere with analyses thereafter. Air may also be introduced into groundwater via the borehole, and this may locally affect the groundwater chemistry.
<table>
<thead>
<tr>
<th>Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| PVC (Polyvinylchloride) and Acrylonitrile Butadiene Styrene (ABS) | • Lightweight 
  • Excellent chemical resistance to weak alkalies, alcohols, aliphatic hydrocarbons, and oils | • Weaker, less rigid, and more temperature sensitive than metallic materials 
  • May adsorb some constituents from groundwater 
  • May react with and leach some constituents from groundwater 
  • Poor chemical resistance to ketones, esters, and aromatic hydrocarbons |
| Polypropylene                     | • Lightweight 
  • Excellent chemical resistance to mineral acids 
  • Good to excellent chemical resistance to alkalies, alcohols, ketones, and esters 
  • Good chemical resistance to oils 
  • Fair chemical resistance to concentrated oxidizing acids, aliphatic hydrocarbons, and aromatic hydrocarbons | • Weaker, less rigid, and more temperature sensitive than metallic materials 
  • May react with and leach some constituents into groundwater 
  • Poor machinability — it cannot be slotted because it melts rather than cuts |
| Teflon                            | • Lightweight 
  • High impact strength 
  • Outstanding resistance to chemical attack. Insoluble in all organics except a few exotic fluorinated solvents | • Tensile strength and wear resistance less compared to other engineering plastics |
| Kynar                             | • Greater strength and water resistance than Teflon 
  • Resistant to most chemicals and solvents 
  • Lower priced than Teflon | • Not readily available 
  • Poor chemical resistance to ketones, acetone |
| Mild steel                        | • Strong, rigid; temperature sensitivity not a problem 
  • Readily available 
  • Low priced relative to stainless steel and Teflon | • Heavier than plastics 
  • May react with and leach some constituents into groundwater 
  • Not as chemically resistant as stainless steel |
| Stainless steel                   | • High strength at a great range of temperatures 
  • Excellent resistance to corrosion and oxidation 
  • Readily available 
  • Moderate price for casing | • Heavier than plastics 
  • May corrode and leach some chromium in highly acidic waters 
  • May act as a catalyst in some organic reactions 
  • Screws are higher priced than plastic screens |

TABLE 2. WELL CASING AND SCREEN MATERIALS (after Discoll, 1986)
<table>
<thead>
<tr>
<th>METHOD</th>
<th>PRINCIPLE OF OPERATION</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drive Point</td>
<td>* small-diameter casing with pointed tip and integral screen is mechanically driven to required depth</td>
<td>* low cost, easy installation sometimes even manually</td>
<td>* no geological samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* water samples can be collected during drilling</td>
<td>* limited to loosely-consolidated formations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* good seal around solid casing in most formations</td>
<td>* difficult to develop, screen easily clogged</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* only metal casing and screen can be driven</td>
</tr>
<tr>
<td>Percussion</td>
<td>* heavy string of drilling tools percsussed into ground with temporary casing driven slightly ahead, drill cuttings removed intermittently with bailer</td>
<td>* suitable for all geological formations</td>
<td>* slow penetration rates especially in hard rock formations</td>
</tr>
<tr>
<td>Jetting</td>
<td>* hydraulic pressure erodes formation and permits penetration of drill rod, drill cuttings brought to surface by return flow</td>
<td>* low cost, easy installation without specialized personnel</td>
<td>* only feasible in limited range of formations, due to penetration problems or formation caving</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* high pressure water-supply required, and even then depth limited to 45 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* poor geological control</td>
</tr>
<tr>
<td>Air Hammer</td>
<td>* reciprocating air hammer connected to drilling bit advancing borehole by pulverising formation, drill cuttings raised by return airflow</td>
<td>* very fast penetration, especially in hard rock formations</td>
<td>* expensive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* only small amounts of water added for temperature and dust control</td>
<td>* rig mobility restricted</td>
</tr>
<tr>
<td>Augering</td>
<td>* unconsolidated formations are cut by rotation of auger of various types and sizes; cuttings are brought to the surface by rotary action of augers</td>
<td>* low cost and fairly simple operation, not needing specialised personnel</td>
<td>* cross-contamination likely</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* rapid set-up clock and moderate penetration rates in some formations</td>
<td>* hazardous if toxic pollution encountered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* no drilling fluid needed especially if core sampling undertaken intermittently</td>
<td></td>
</tr>
<tr>
<td>Hydraulic</td>
<td>* rotating drilling bit penetrates formation and cuttings brought to surface by drilling fluid (mud/water/air) which can be recirculated after settlement of cuttings</td>
<td>* rapid penetration in most geological formations</td>
<td>* depth limited to about 40m in favourable conditions above groundwater table</td>
</tr>
<tr>
<td>Rotary</td>
<td></td>
<td>* practically unlimited depth capacity depending on rig size</td>
<td>* not suitable for rock or gravel formations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* core sampling can readily be undertaken</td>
<td>* smearing of borehole walls makes development difficult</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* cross-contamination of water samples very likely</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* expensive and requires skilled operator and many accessories</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* contamination of samples by drilling fluid and from higher levels in borehole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* geological control can be poor if no core sampling undertaken</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* use of drilling mud has numerous advantages but presents borehole</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>development problems</td>
</tr>
<tr>
<td>Reverse</td>
<td>* similar to hydraulic rotary, except that drilling fluid is always water, which circulates down the borehole outside, and rises inside, the drill stem (the reverse to the standard rotary method)</td>
<td>* produces a very clean, well-developed borehole</td>
<td>* large water-supply needed, especially for boreholes in deep permeable formations</td>
</tr>
<tr>
<td>Rotary</td>
<td></td>
<td>* suitable for all geological formations to considerable depths</td>
<td>* expensive and requires skilful operator and many accessories</td>
</tr>
<tr>
<td></td>
<td></td>
<td>* split-spoon core samples can be taken intermittently during drilling</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* minimum borehole diameter about 45mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* cross-contamination of water samples very likely</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>* poor geological control</td>
</tr>
</tbody>
</table>

**TABLE 3. COMPARISON OF DRILLING METHODS** (after Foster & Gomes, 1989).
Borehole design depends on the location and number of horizons needing to be monitored. Several screened lengths in a single string can be inserted into a borehole, but the risk of cross contamination between screened lengths and cross-flow behind the casing as well as the need to use packers to isolate the sampling zones renders this system least desirable. One alternative is to place nests of monitoring boreholes in a single drilled borehole with a hydraulic seal placed between each zone (Figure 2). The best method is to place carefully structured monitoring boreholes to strategic depths with a short length of screen open to the zone of interest. These can either be placed singly or in clusters to monitor different depths at selected locations (Figure 3). Further details are available in Driscoll (1986) and Barcelona et al., (1985), but single completion boreholes are preferable to nests because of the danger of cross-contamination between sampling zones.

The selection of locations for monitoring boreholes and the depths to proposed sampling points depends on a good understanding of the prevailing groundwater regime. Monitoring point-source pollution requires prediction of groundwater flow-paths and velocities and pollution transport. Monitoring boreholes, therefore, need careful siting and design to fulfil their role.

2.2.3.2 Controlled Grab Sampling and Specialised Equipment

A variety of bailer samplers are described in Section 2.2.2.2 and these and other sampling devices are summarised in Table 4. They include ball-valve type bailers (Figure 4), the bladder pump (Figure 5), suction lift (Figure 6), gas lift pump (Figure 7) or peristaltic pump (Nielson and Yeates, 1985). Care should always be taken to avoid cross-contamination between boreholes via the sampling equipment.

The bladder pump provides efficient well-purging and enables representative samples to be collected over a range of conditions. Grab samplers may include the conventional bailer, dual-check valve bailer and syringe pump; they are unsuitable for well purging and require careful handling. The peristaltic pump is suitable for depths down to 6 m only; a loss of determinand may arise for some organic compounds.

There are a number of innovative sampling devices described in the literature which satisfy the peculiar requirements of particular determinands. For example, Gillham (1982) and Pankow et al., (1984) describe a remotely operated syringe for obtaining samples for organic analysis, and Eminhisar and Singh (1984) describe a number of other techniques. A foot valve on a length of tubing forms an inertial pump when the tube is rapidly moved up and down. The inertial pump has been successfully used up to a head of 50 m (Rannie and Nadon, 1988).

Depth samples taken from the column of water within a borehole represent groundwaters whose origin can only be crudely defined by means of borehole geophysics and a thorough knowledge of the prevailing groundwater regimes. Flowmeter, conductivity and temperature logging (in conjunction with caliper and electric logs in uncased boreholes) carried out, both when the borehole is pumped or static, enables the most likely sources of groundwaters to be located.

Flowmeter logs measure the upward (or downward) velocity of water in the borehole column; conductivity logs define the specific electrical conductance of the water column, and temperature logs show variations in groundwater temperature within the borehole. The caliper log measures the borehole diameter at any given depth and helps to identify cracks, joints and other
FIGURE 2. Multiple Completion well cluster (after Morrison, 1983).

<table>
<thead>
<tr>
<th>Sampling Devices</th>
<th>Approximate Maximum Sample Depth</th>
<th>Minimum Well Diameter</th>
<th>Sample Delivery</th>
<th>EC</th>
<th>pH</th>
<th>Redox</th>
<th>Major Ions</th>
<th>Trace Metals</th>
<th>Nitrate</th>
<th>Fluoride</th>
<th>Dissolved Gases</th>
<th>Non-volatile</th>
<th>Volatile</th>
<th>TOC</th>
<th>TOX</th>
<th>Radon</th>
<th>Gross Alpha &amp; Beta</th>
<th>Coliform Bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom sealed bailer</td>
<td>no limit</td>
<td>12 mm</td>
<td>variable</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top and bottom valve</td>
<td>no limit</td>
<td>12 mm</td>
<td>variable</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syringe sampler</td>
<td>no limit</td>
<td>38 mm</td>
<td>0.05-1 l</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Bladder pump</td>
<td>120 m</td>
<td>38 mm</td>
<td>0-0.15 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Helical rotor</td>
<td>48 m</td>
<td>50 mm</td>
<td>0-0.08 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piston pump (gas driven)</td>
<td>150 m</td>
<td>38 mm</td>
<td>0-0.04 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugal</td>
<td>variable</td>
<td>75 mm</td>
<td>variable</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peristaltic</td>
<td>8 m</td>
<td>12 mm</td>
<td>0-0.02 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Gas-lift</td>
<td>variable</td>
<td>25 mm</td>
<td>variable</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>Gas-driven</td>
<td>45 m</td>
<td>25 mm</td>
<td>0-0.01 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In situ Pneumatic</td>
<td>no limit</td>
<td>not applicable</td>
<td>0-0.01 l/s</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
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**TABLE 4. SUMMARY OF SAMPLING DEVICES AND THEIR APPLICATIONS** (after Pohlmann and Hess, 1988).
FIGURE 4. A PVC ball valve sampling bailer.

FIGURE 5. Schematic diagram of bladder pump (after Stuart, 1984)
FIGURE 6  A simple suction lift sampling system (after Sinton, 1983).

FIGURE 7. An air/gas lift sampler.
areas of weakness that may intersect the borehole. Electric logs indicate certain physical properties of the rock and groundwater adjacent to the borehole. Upward or downward flow may occur naturally between zones of different head, and depth samples may be located at influent zones in order to identify discrete groundwater types entering the borehole.

2.2.3.3 Packer Sampling

The use of borehole packers enables discrete zones of particular hydraulic significance to be isolated for sampling. A packer comprises two inflatable seals which are lowered to straddle a particular zone of interest within a borehole, and inflated in order to isolate that zone hydraulically. This provides a greater degree of control over the sample source than is allowed using depth samplers. Packers may either be located temporarily whilst a particular sample or suite of samples is collected or they may be permanently installed (Figure 8).

A variety of commercially available internal casing packer systems is available. These may be lowered, inflated, deflated, and raised to enable samples to be collected from discrete zones. External casing packer assemblies may be used on a permanent basis to isolate specific zones in a borehole (Figure 9). A special tool is necessary to open and close access ports to each zone (Patton, 1979).

2.2.3.4 Pore-Water Extraction from Cores

Pore-water may be recovered from core in order to obtain a precise log of groundwater chemistry with depth. However, care must be taken to avoid contamination of the pore-water by fluids used in the drilling process. Air-flush or percussion coring methods of drilling are preferable.

Lithium chloride (LiCl) tracer may be added to the drilling fluid to check on fluid invasion. In the English Chalk, Edmunds and Bath (1976) demonstrated core invasion to a depth of 1.0 to 1.5 cm, but in the Permo-Triassic sandstones of Cumbria it was greater. The use of a tracer in drilling fluids is always desirable, and sub-sampling of the inner axial part of the core provides least contaminated material.

Rotary coring devices include conventional core barrels and thin wall tube samplers (Figure 10). The hollow-stem auger is suitable for sampling shallow depths in unconsolidated material and dry percussion driven samplers such as U100's (100 mm diameter tubes) can be used in unconsolidated sediment and in consolidated Chalk.

Extraction of pore-water should be rapid and preferably carried out on site, otherwise fractionation, denitrification and TOC degradation of the interstitial water may occur. Core samples may be stored in thin walled sample tubes with the ends sealed in wax, or they may be extruded from the core barrel or tube and coated in wax, aluminium foil and polythene.

Pore-water extraction is generally undertaken by centrifugation. Either the water is allowed to drain freely through a porous plate supporting the sample and collected in a cup at the bottom of the centrifuge tube or an excess of dense immiscible liquid (e.g. Arklone P (ICI Limited) is added to the sample and the displaced water collected after it has floated to the top (Kinniburgh and Miles, 1983). Centrifugation may be carried out in an inert atmosphere if required. In the case of mudrocks, squeezing in a triaxial cell to extract pore-water may be effective.
(a) isolation of one zone for sampling within a borehole

(b) 4-packer system for sampling central zone of three

FIGURE 10. Thin wall tube sampler.
The representativeness of centrifuge extracted pore-waters was tested by Kinniburgh and Miles (op. cit.) who demonstrated that little analytical variation was observed between samples which were subject to centrifugation for a range of times and speeds.

Sampling for organic compounds (e.g. pesticides) may be carried out by solvent extraction or headspace methods. The solvent extraction technique requires solvent to be mixed with crushed core samples and removed by centrifugation. The headspace technique is the removal of volatile vapours from crushed core samples. This is done by incubating the sample at 70°C to drive vapour into a confined headspace from which vapour samples can be collected by syringe.

2.2.3.5 In-Situ Sampling

A number of in-situ sampling devices are available for permanent installation in a borehole which may then be backfilled with inert permeable material incorporating bentonite seals between sampling zones (Norman, 1986). The Water Research Centre in-situ sampler uses compressed inert gas to lift the sample to surface (Figure 11). The device may clog with sediment and bacterial colonies may develop in time. The main advantages of gas-drive samplers are cost, they allow groundwater level measurements to be made, and they require minimal purging, disadvantages are that sampling of large volumes is time consuming, it is not suitable for immiscible pollutants, and the sampler cannot be retrieved or replaced. Nitrogen is commonly used as the inert gas to drive the systems.

2.2.3.6 In-Situ Measurements

Measurement of certain parameters can be carried out within the borehole column. This may be carried out by normal geophysical logging techniques or by a probe permanently installed in rising mains or monitoring boreholes. In addition to conductivity and temperature logs, sondes are available to make point measurements of dissolved oxygen. Eh and pH within the borehole column, and work is being carried out on the measurement of nitrate, ammonium and chloride (Harrar and Rober, 1982). The development work is hindered by the need to work at high pressures with remote interrogation of the probe.

In-situ measurement of certain volatile organic compounds, notably the chlorinated hydrocarbons, can be undertaken with down-hole sorption cartridges. The cartridges utilize adsorption media such as activated carbon or resins from which contaminants can be eluted in the laboratory once they are recovered from the borehole (Pankow et al., 1984).

2.3 UNSATURATED ZONE SAMPLING

The unsaturated zone holds large volumes of water under surface tension in the porous matrix, which also contains varying proportions of gas. In the case of the Chalk, the pore sizes are so small that the matrix is virtually saturated. Below the zone of influence of plant roots the movement of this water will be predominantly downwards. This is the water which will recharge the aquifer in the future and its quality will affect the quality of the groundwater once it reaches the saturated zone. Monitoring of the unsaturated zone, therefore, provides an early warning of incipient groundwater contamination from diffuse or point-sources such as leached nitrate and pesticides or landfill sites and soakaways.
FIGURE 11. Permanent sampling installations.

FIGURE 12. Cross-section of a typical pressure-vacuum lysimeter.
The British aquifers, notably the Chalk, have relatively thick unsaturated zones (more than 20 m and up to 50 m) and surface-derived pollutants can remain in this zone for decades. For the most part, the soils developed over the outcropping aquifer are thin, highly permeable and well aerated, and they allow rapid infiltration of excess rainfall to the unsaturated zone.

2.3.1 Pore-Water Sampling

The methods and procedures used for sampling pore water in the saturated core (Section 2.2.3.4) generally apply in the unsaturated zone. Unconsolidated sediments are best obtained with a hollow-stemmed continuous flight auger, or undisturbed percussion core sampler, with the borehole wall supported by drive pipe above each sample interval.

The advantages and disadvantages of the direct pore-water sampling methods are summarised by Wilson (1983). Core samples are best obtained by the undisturbed (100 mm diameter) core sampler dry tube (U100) to minimise contamination, but it is an expensive procedure.

2.3.2 Suction Sampling from Tensiometers

The use of a porous ceramic cup placed under vacuum for collecting water in the unsaturated zone (Figure 12) was first described by Wagner (1962). A porous cup mounted on the end of a piezometer tube and placed under vacuum will slowly suck water percolating through the unsaturated zone into the cup. The water may be periodically raised to the surface under suction, by gas-lift or other means. Only small volumes can be obtained in this way.

The validity of the samples derived from suction tensiometers was described by Hansen and Harris (1975), who found a 60% range in sample concentration derived from eight different samplers in a small uniform plot. Sample bias may occur due to sorption, leaching, diffusion, and the drainable soil-water concentration. The sampling technique and sampler design should be standardised within any one project. The ceramic cup should be buried in silica sand to provide an adequate hydraulic contact wherever coarse-grade material is present.

Shallow sampling (e.g. in the soil zone) may also be carried out using pan lysimeters. These are small collection trays driven horizontally from the sides of a trench in order to intercept percolating water (Parizek, 1970). This technique induces less bias to the water samples than does suction tensiometers but is confined to the depth of a trench.

2.4 SPRING SAMPLING

Springs offer a useful source of groundwater which is discharging naturally from an aquifer. Perennial springs are likely to represent effluent from deeper, larger aquifers, whereas seasonal springs may drain superficial gravels, or, in the case of the Chalk and other fissured aquifers, represent temporary discharge at higher elevations than normal due to seasonal or short-term recharge. For the most part the flow paths of water leading to a spring are not known and the source represents a mixture of groundwaters whose origin can only be described in general terms. Care should be taken to check if field drains contribute to a source. Nevertheless, spring sources provide a valuable means of collecting "bulk" groundwater samples.
Spring samples should be obtained directly from the spring orifice in order to avoid contamination at the surface from, for example, sediment and vegetation. Contact between water and air will probably have modified any reducing characteristics of groundwater before it appears at surface, but tubing can be pushed into small sources to draw least affected spring water.
3. SAMPLING PROCEDURES FOR DIFFERENT DETERMINANDS

As soon as a sample of fluid is removed from either the saturated or the unsaturated zone of an aquifer, it is subject to chemical and physical changes. The range of stability of determinands varies greatly from highly stable major ions (e.g. Cl) to dissolved gases which are released rapidly on sampling due to reduced pressure (Table 5). Changes to the environment of the sample should be minimised by selecting the most suitable sampling method for the determinand, or group of determinands being investigated (Section 2). Samples are subject to changes in pressure, temperature and light and may be oxygenated when brought into contact with the atmosphere. These changes are likely to seriously alter the concentration of some of the determinands being monitored and steps need to be taken to control and reduce these effects.

In order to measure concentrations of determinands that are representative of the in-situ values, it may be necessary to carry out analyses on site, either using an in-line cell, to prevent contact with the atmosphere, or shortly after the sample has been collected. Where measurement of determinands requires sophisticated laboratory equipment or where physical-chemical changes are not rapid then samples can be filtered and preserved in non-reactive containers for transport to the laboratory. The time interval between sampling and analysis can be extended, in some instances, by sample preservation methods, such as acidification, to keep metals in solution and chilling to slow down other reactions.

Before embarking on a sampling programme it is therefore important to define the determinands to be investigated and prepare suitable sampling procedures accordingly (Section 1). All available data relating to the hydrogeological environment and the completion of the well or borehole should be studied prior to sampling, in order to assess any likely influence on the groundwater chemistry. The method of groundwater sampling should then be chosen, depending on the determinands to be measured and the constraints imposed by availability of the equipment etc. Finally, the programme of sample collection, method of filtration, preservation and storage require definition in order to obtain representative samples for analysis.

3.1 LIQUID PHASE

The liquid phase is sampled to permit measurements of dissolved ions, isotopes and unstable determinands such as dissolved gases, relatively low-solubility determinands such as the many organic compounds, and for microbiological populations.

Concentrations of determinands can change during sampling and different determinands require specific methods of collection, preservation and storage. The methods of preservation and the volume required for analysis can vary depending on the method of field or laboratory analysis. Most texts on groundwater sampling contain lists of determinands and recommended methods of collection, preservation, storage and analysis.

Some of the more recent and comprehensive sampling recommendations are contained in Scaife et al. (1981), APHA (1981) and SCA (1980). The last two sets of recommendations are critically compared by Hunt and Wilson (1986) who emphasise the problems involved in recommending stabilisation procedures suitable for a wide range of determinands. In general, the specific recommendations vary little, except where different methods of analysis are used. An example of this is the use of acid to stabilise metals in solution: APHA recommend using nitric acid (HNO₃) to reduce pH to less than 2 whereas
SCA recommend adding 2 ml of 5M HCl per litre of sample or 2-10 ml HNO₃ per litre of sample. The recommendations for sampling and preservation of samples for a large range of determinands as detailed in the General Principles of Sampling and Accuracy of Results (1980) compiled by the SCA are reproduced in Appendix 1. The International Standards Organisation is currently preparing detailed recommendations for stabilisation procedures.

3.1.1 Purging of Sampling Installations

Before collecting samples from pumped boreholes it is necessary to ensure the sample is representative of the water in the aquifer and not self-contaminated by corrosion of borehole casing, pollution from the wellhead etc. Anomalous, often stagnant, water requires "purging" from monitoring boreholes and the volume of water to be removed is usually calculated by rule-of-thumb guidelines such as 3, 5 or 10 borehole-volumes.

Barcelona et al., 1985, consider that these rule-of-thumb guidelines can be a liability in terms of time and expense and recommend that the volume to be pumped should be calculated from consideration of the known aquifer properties.

The time taken to purge a borehole until it produces (say, 95%) aquifer water is related to aquifer transmissivity, and casing diameter (effectively borehole storage) but not pumping rate when the pump intake is in the screened or open section of the borehole. Shortest purging times can be expected in small diameter boreholes in highly transmissive aquifers. Purging times are obviously increased if the pump is in the cased section of the borehole when the column of water between the pump intake and the top of the screen or open hole must be purged prior to sampling.

Using equations derived by Papadopoulos and Cooper (1967) for analysis of pumping test data in boreholes with finite storage, Gibb et al. (1981) derived a set of curves relating percentage aquifer water to purging time for a specified discharge rate and transmissivity and variable casing diameter (Figure 13a). Barcelona et al. (1985) produced a similar set of curves for a fixed discharge and casing diameter but for a range of transmissivities (Figure 13b). These figures are comparable only along the curves representing 51 mm casing diameter (Figure 13a) and 2.5 m²/day transmissivity (Figure 13b). Comparison at selected "per cent aquifer water" values shows no reduction in purging times resulting from a nearly 10-fold increase in pumping rate. These types of calculations should be used only as guidelines to purging times and the effect of the position of pump relative to the screened section or productive zone must be taken into account (Section 2.2).

The calculated purging time is best verified by in-line monitoring of the water quality in a flow-through cell (Figure 14). One or more parameters can be monitored, including redox potential (Eh), dissolved oxygen content (D.O.), pH, temperature (t) and conductivity (Ω⁻¹). Stability is considered to have been achieved, and hence representative aquifer water obtained, when the selected parameters vary by less than 10% over two successive well volumes or appropriate time period. Eh, D.O. and t must be measured in the flow-through cell to avoid contact with air and to minimise temperature change, but pH and Ω⁻¹ can be determined on samples collected at regular intervals.

Once the purging of a well is complete, the pumping rate should be decreased prior to sampling for the predetermined suite of determinands. On-site analysis of the monitoring parameters (Eh, pH, DO, t and Ω⁻¹) is recommended and additionally bicarbonate (HCO₃). Volumes of sample, both
FIGURE 13. The relationships between percentage aquifer water to time of purging in a well (after a) Gibb et al., 1981, and b) Barcelona et al., 1985).

filtered and unfiltered, are then collected either with or without the addition of a suitable preservative.

3.1.2 Filtration of Samples

Groundwater samples, particularly those collected by depth sampler, may contain suspended solids which if not removed, can influence analytical results. Reactions between the water and suspended solids may include ion-exchange and dissolution of particulate and colloidal material. Additionally, sample acidification may dissolve suspended solids and produce misleading results.

Filtration is recommended in most instances even when no suspended solids are apparent. However, it is advisable to refrain from filtering samples for total organic carbon (TOC), or other organic compounds as increased handling may result in loss of the determinand of interest (Barcelona et al., 1985).

Filtration should be carried out in the field, before preservation, preferably using an in-line filtration unit which utilises the sampling pump pressure. Where this is not possible a pressure filtration unit should be used, preferably using nitrogen to drive the system but compressed air from a hand/foot pump is also acceptable in most circumstances (Figure 15). For small volumes a syringe fitted with a filter is recommended. Vacuum filtration sampling devices are not recommended as they encourage loss of dissolved gases and volatile compounds.

Selection of a filter depends on the determinands to be investigated but, in general, a cellulose-acetate filter with a 0.45 μm pore-size is recommended. The filter will permit the passage of some bacteria and colloidal material but smaller pore sizes will tend to clog rapidly. If the sample is turbid a coarse glass fibre pre filter may be used.

The choice of filter medium is related to the determinand being investigated and clearly, if organic solvents are likely to be encountered, organic filter media (cellulose nitrate, cellulose acetate or polycarbonate) should not be used. In these cases, glass-fibre or PTFE (Teflon®) filter media are recommended (Barcelona et al., 1985). Further detailed discussion of selection of filter media and the problems associated with different types is given by Hunt and Wilson (1986) (Chapter 11.2.1) where problems such as contamination arising from the filter material and losses due to absorption are discussed. The filtrate should be collected in a large container before subsampling as progressive clogging of the filter may progressively change the nature of the filtrate.

3.1.3 Sample preservation

Preservation of samples is required for determinands that may change in concentration in the time between collection and analysis. Preservation commonly involves adding acid to lower the pH to about 2, preventing the precipitation of metals, followed by storage at 4°C to slow chemical and organic reactions. Methods of preservation for different determinands are given in Appendix 1, which is based on SCA(1980), amended to include determinands of special interest in groundwater investigations. Many determinands have common preservation techniques so they can be collected and stored in the same container. If possible, transport to the laboratory and subsequent storage prior to analysis should also be at 4°C. Recommended maximum storage times for different determinands vary considerably from 24
hours to 6 months and these times should be taken into account when planning a sampling or monitoring programme. Times derived from Scalf et al. (1981), and Barcelona et al. (1985) have been added to Appendix 1.

3.1.4 Sample collection

Many groundwaters have low dissolved oxygen (DO) content so it is important to collect samples with the least disturbance and aeration, and to fill the bottle to the brim. For most samples, polyethylene or glass containers with water-tight caps are suitable but where the material may increase or decrease the concentration of determinands, special containers must be used.

Flowed or pumped samples should be collected as close as possible to the pump with the minimum intervening pipework, header tanks etc. If collected from an existing tap, ensure that leaks do not contaminate the sample (Swinton, 1986) by using an S-bend hose if necessary (Figure 16).

The sample container should be rinsed thoroughly with a portion of the sample, filtered or unfiltered. Where an in-line cell has been installed to monitor changes in pH, Eh, D.O. Q^{-1} and t during the purging process, a T-junction should be fitted upstream to facilitate sample collection.

The sample collection programme will be defined by the determinands under investigation, and the on-site treatment and preservation requirements will also be controlled by the proposed method of analysis. Using the detailed list of sample collection and preservation techniques and storage times in Appendix 1, a sample collection programme can be devised. For a "typical" groundwater sampling exercise involving the determination of the major inorganic and organic determinands the procedure in Figure 17 should be followed. The volume of sample collected is determined by the method of analysis to be used and should be selected in consultation with the laboratory carrying out the analyses.

Quality control (QC) of analytical results in groups of laboratories is discussed in great detail by Hunt and Wilson (1986), who also highlight some of the problems introduced by sampling methods. Barcelona et al. (1985) recommend the use of field blanks, standards and spiked samples for effective QC to account for changes in samples which occur after collection. The authors specify concentrations of field standards and sample spiking solutions for different sample types (Table 2.10, page 67). Field blanks and standards enable systematic errors arising from handling, storage, transport and laboratory procedures to be quantified and corrected. These QC measures will help ensure that data are collected with a known degree of accuracy. This is particularly important in long-term monitoring programmes where different personnel, and even organisations, may be involved in sample collection and analysis.

3.1.5 Low-Solubility Determinands

Previous discussion has related to sampling groundwater for either natural or contaminant determinands that are soluble in water and hence part of the groundwater body. However, a large number of pollutants have low-solubility in water and have a range of densities and volatilities, resulting in variable mechanisms of transport through the unsaturated zone to the saturated zone. Here a discrete plume will form, whose shape is controlled by the local groundwater flow regime.
FIGURE 16. Collection of an uncontaminated sample from a leaking tap (after Sinton, 1986)
FIGURE 17. Flow chart for optimal collection of groundwater sample for analysis of common determinands.
Plumes of low-solubility pollutants result from localised waste disposal or spillages and can take the form of either a "pancake" on the groundwater surface or, if more dense, on the confining layer at the base of the aquifer. Lawrence and Foster (1987) discuss the transport of immiscible fluids in both the unsaturated and the saturated zones of an aquifer. In the latter zone, the transport of the fluids is controlled, not only by the groundwater flow, but also the density and viscosity of the fluids. Hypothetical pollution plumes resulting from the introduction of relatively low and high-density fluids are shown in Figure 18. In practice, the shape of the plume will be modified by the nature of the aquifer and will vary considerably, particularly in fissured aquifers.

Sampling from boreholes should be approached with great caution as the stratified column of fluids in a borehole may not represent the stratification in an aquifer due to density differences especially if saline water is present at depth. Pumped samples may not be representative and depth samples are liable to be contaminated by overlying layers.

Sampling of purgable organic compounds (POC's), present special problems because of their low molecular weights, low solubilities in water, low boiling points and their tendency to volatile loss in open systems. Imbrigiotta et al. (1988) evaluated seven sampling devices in an experimental field situation and found significant differences among the mean concentrations of POCs determined with different devices. The highest precision was obtained from the positive-displacement pumps and lowest precision from depth-sampling devices.

Special precautions need to be taken where highly volatile hydrocarbons may be encountered, to avoid fire and explosion. Careful selection of materials for piezometer construction, pumping systems and sample containers must also be made. In such cases materials such as PTFE (Teflon®) and stainless steel are needed to avoid interaction with the contaminant being sampled.

### 3.1.6 Microbiological Populations

It may be necessary to sample microorganisms in an aquifer, either to determine the presence of pathogens or indicator organisms in a water supply or to investigate the occurrence and/or behaviour of indigenous bacteria. Pathogens include a variety of bacteria and viruses responsible for waterborne diseases, such as gastroenteritis, cholera and typhoid fever. Indigenous bacteria are responsible for microbial transformations of organic and inorganic compounds in groundwater and include denitrifiers, sulphate reducers and methanogens.

The purpose of the sample determines the type of sampling procedure. For water-supply quality surveillance in relation to pathogens, it is usual for a water sample to be collected from a well, borehole or spring. In order that the sample be representative, their location, construction and completion must be taken into account and care exercised to avoid contamination during the sampling process. A sterile sampling bottle should be used and care taken not to contaminate the stopper or mouth of the bottle.

Wells, boreholes and springs provide numerous habitats for microbial colonisation and it is essential that standing water is removed prior to sampling. If the sample is collected from a well in which a pump is already installed it is advisable to collect the sample as close to the pump outlet as possible in case the wellhead distribution system is colonised by bacteria. The sample tap should be disinfected or sterilised by flaming prior to
FIGURE 18. Pollution plumes resulting from fluids of different densities (after Lawrence and Foster, 1985).
sampling. When an open well is being sampled either using a bailer or portable pump, an attempt should be made to disinfect the equipment or at least to handle it with care to avoid gross surface contamination.

Both indigenous microbes and pathogens will be often be attached to aquifer surfaces and therefore groundwater samples may not accurately reflect the subsurface population. For this reason, samples of subsurface solids are of interest, and essential for the study of indigenous populations in particular. Core may be obtained by a variety of drilling techniques minimising the use of drilling fluid which increases the risk of contamination. The outer portion and ends of each core length should be discarded and samples for microbiological analysis taken from the inner portion using sterile equipment. The disadvantage of solid sampling is that it is both expensive and destructive.

Enteric viruses may be present in sewage and may be transferred to groundwater from septic tanks, leaking sewage lines, domestic and sludge landfills, land disposal of sewage effluent, leaking sewage ponds etc. Gerba (1988) describes the problem, stresses the need to detect viruses in groundwater and describes sampling and analytical methods. Viruses that may be present in sewage are listed in Table 6, together with some of the wide variety of diseases in man that they can cause. Because of the high risk associated with enteric viruses the maximum recommended level in drinking water is zero.

Viruses need to be detected in water supplies independently of coliform bacteria, which are currently used to judge microbial safety of drinking water, because studies by Marzouk et al. (1979), and Slade (1985) have shown that viruses can be present in the absence of coliform bacteria.

The potential health significance of small viral populations in water demands that large samples (40 to 1000 litres) are collected and concentrated by adsorption onto microporous filters. Two types of filters are used: electronegative and electropositive. The former type has been demonstrated to have a greater capacity for virus adsorption in waters with high turbidities and organic matter, but the water requires pretreatment prior to filtering which can be cumbersome in the field. As groundwaters are generally of low-turbidity, electropositive filters are more convenient for field use as no pre-treatment of the water is required if the pH is 8.5 or less (Gerba, 1988).

Viruses concentrated on the filters can be removed for analysis, either in the field or at the laboratory by elution. Virus analysis is both time consuming and costly but the use of the recently developed electropositive filters enables sample collection by personnel with a minimum of training. Further reductions in costs are being achieved by improved laboratory methodology, particularly the recent development of gene probes for virus detection (Gerba, 1988).

3.2 GASEOUS PHASE
In the saturated zone, gases occur in their dissolved forms in the groundwater. Naturally occurring dissolved gases most commonly include oxygen, methane and carbon dioxide, and their concentration is controlled by availability and pressure. Dissolved nitrogen can also occur in groundwater as a result of denitrification of nitrates introduced into aquifers from diffuse sources.

Sampling for dissolved gases in groundwater must be carried out without reduction in pressure which will rapidly result in degassing. This can be
<table>
<thead>
<tr>
<th>Viruses</th>
<th>Type</th>
<th>Diseases Caused</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enteroviruses</td>
<td></td>
<td>meningitis, paralysis, fever</td>
</tr>
<tr>
<td>Poliovirus</td>
<td>31</td>
<td>meningitis, diarrhoea, rash, fever respiratory disease</td>
</tr>
<tr>
<td>Coxsackievirus A</td>
<td>23</td>
<td>meningitis, herpangina, fever</td>
</tr>
<tr>
<td>Coxsackievirus B</td>
<td>6</td>
<td>myocarditis, congenital heart anomalies, pleurodynia, respiratory disease, fever, rash meningitis</td>
</tr>
<tr>
<td>New enteroviruses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Types 68-71)</td>
<td>4</td>
<td>meningitis, encephalitis, acute haemorrhagic conjunctivitis, fever, respiratory disease</td>
</tr>
<tr>
<td>Hepatitis Type A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(enterovirus 72)</td>
<td>1</td>
<td>infectious hepatitis</td>
</tr>
<tr>
<td>Norwalk virus</td>
<td>1</td>
<td>diarrhoea, vomiting, fever</td>
</tr>
<tr>
<td>Calicivirus</td>
<td>1</td>
<td>gastroenteritis</td>
</tr>
<tr>
<td>Astrovirus</td>
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<td>gastroenteritis</td>
</tr>
<tr>
<td>Reovirus</td>
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<tr>
<td>Adenovirus</td>
<td>40</td>
<td>respiratory disease, eye infections, gastroenteritis</td>
</tr>
<tr>
<td>Rotavirus</td>
<td>4</td>
<td>diarrhoea</td>
</tr>
<tr>
<td>Snow-Mountain Agent</td>
<td>unknown</td>
<td>gastroenteritis</td>
</tr>
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**TABLE 6.** Human enteric viruses which may be present in sewage. (after Gerba, 1988).
achieved either by sealing a sample in a device in-situ in a borehole, or by pumping a sample to the surface. Pumped samples should be collected in a glass flow-through container which, after flushing with the sample, is sealed firstly at the outlet-end and then at the inlet-end to maintain the pressure.

Sampling for gases in the unsaturated zone of an unconfined aquifer or the dewatered zone of a confined aquifer is commonly carried out to detect methane in order to evaluate potentially explosive situations. When part of a naturally confined aquifer has been dewatered by pumping, gases can be sampled by vacuum pumping, providing an effective seal to the atmosphere can be ensured in and around the borehole casing. Alternatively natural "pumping" of the gases in the unsaturated zone will occur in aquifers with a confining layer when atmospheric pressure declines and causes a corresponding rise in groundwater level. This phenomenon has long been known and can result in an accumulation of "bad air" in restricted spaces and buildings around wellheads. In Chalk aquifers the gas is commonly carbon dioxide which can cause asphyxiation but in other geological situations methane can accumulate.

Methods for measurement of the gaseous phase at shallow depth have developed rapidly in recent years because of the demand created by investigation of groundwater contamination with volatile organic compounds (VOCs). These compounds are commonly detected in the unsaturated zone using portable gas chromatographs or photoionisation detectors. The application of these portable detectors is economical, but in some cases does not provide for adequate species differentiation (Voorhees et al., 1988). The authors suggest that compared with instantaneous collection methods, time integrated collection techniques yield statistically superior results. These samples are collected using economical static collectors which are buried in augered holes to a depth of about 45 cm and left to equilibrate with soil vapours for 7-30 days. After the integrated collection period, the devices are retrieved for laboratory analysis by Curie-point desorption mass spectrometry which allows the detection and identification of compounds up to mass 240. The results can be interpreted by mapping the relative ion count (flux) of the identified compound and hence the extent and apparent direction of migration of the contaminant plume can be determined.

A new technique for monitoring pollutants in the soil (gaseous) as well as in groundwater involves the use of in-situ fibre-optic chemical sensor (FOCS) coupled with the new technology of remote fibre spectroscopy (RFS) (Stanley et al., 1988). FOCS monitor single pollutants and the fibre connecting it to the surface is used to transmit both the optical stimulus to the sensor and the return signal, which is spectroscopically analysed. Bundles of fibres will be required to monitor a number of compounds at a variety of depths but as the diameter of the fibres is 100 to 200 μm, a very small hole will need to be punched or drilled.

3.3 SOLID PHASE

A detailed description of techniques for sampling the solid phase is outside the scope of this manual. However, knowledge of the nature of the rock through which groundwater travels is required in any hydrogeochemical evaluation, not only for assessment of the hydraulic regime, but also the solid phase geochemistry and the resultant water-rock interactions.

Samples of rock can be obtained by a variety of drilling methods, ranging from hand-augering at near-surface sites to percussion or rotary core drilling to collect samples for specified analyses. Sampling for pore-water analysis in
both the saturated and unsaturated zones has been described in Section 2, which emphasises the need to avoid contamination by the drilling process.

Care must be taken to collect and preserve solid samples required for analysis. The change of environment upon extraction can result in geochemical changes which must be minimised in the period between collection and analysis. The main changes that can affect core are physical damage by the drilling process, deterioration due to pressure release, dehydration (particularly clays) and oxygenation upon contact with the atmosphere. To minimise these effects the core should be wrapped in plastic immediately upon removal from the core barrel and stored at $4^\circ$C to inhibit chemical and microbiological reactions. SCA (1983) recommend storage of solid samples at $-18^\circ$C, but this would only be advisable in the case of geological samples of disaggregated material, since the fabric of solid cores could be destroyed by the freeze-thaw effects on pore waters.

Percussion coring using U100 tubes driven into the rock to collect samples is an especially effective method of gathering uncontaminated samples. When further refined by using a rigid plastic liner, minimal contamination occurs. On recovery, about 20 mm of core is removed from each end of the sample to make space for a hot wax seal prior to storage. An additional advantage of the method is that the core can be inspected and subsampled at a later date by either extrusion or by cutting both the core and the plastic liner in the manner most suited to the demands of the sampling method.
4. CONCLUSIONS

It is essential to identify the objectives of a groundwater monitoring programme from the outset. This will determine the required parameters for analysis, the proposed sampling installations and the scope of the monitoring network and the required level of funding. Typical objectives may include advanced warning of approaching pollutants, changes in groundwater quality due to changing land use or changing climate or the distribution of contaminants in an aquifer.

Once the objectives of a groundwater monitoring programme have been defined, the sampling strategy needs to be designed to meet these objectives. The strategy should incorporate a quality assurance programme and may involve an initial intensive phase of sampling to define key parameters for monitoring in the longer term.

Selection of sampling points, either existing or specially constructed, requires a detailed knowledge of the regional hydrogeology and the local flow regime, particularly where affected by pumping. A knowledge of borehole completion is also required and, in some cases, the flow regime in a borehole can determine the level at which samples should be collected.

Traditional sampling methods such as grab sampling in static boreholes and bulk sampling of pumping boreholes are of limited value. The depth and origin of these samples is generally unclear and loss of volatile substances is likely. Improved sampling techniques are available and their application depends on the balance between increased cost and increased value of the data so obtained.

Aquifer surveillance traditionally depends on samples collected from production boreholes. Samples obtained from long-screen and open-hole boreholes may represent a cocktail from many horizons and mixtures may vary with pumping rate, duration of pumping and other factors. Preferably, sampling should be collected from clusters of single short-screen monitoring boreholes, each drawing on a single horizon with no opportunity for cross-contamination within the borehole. Such clusters should be introduced to regional monitoring programmes as control points in addition to selected production borehole sites for which long standing time-series data are available. Monitoring clusters should be sampled periodically with appropriate portable sampling equipment.

The process of collecting a sample of groundwater usually alters its physical and chemical environment. Changes to the sample can be minimised by on-site analysis, careful preservation of the sample or use of specialised sampling methods such as collection of pressurised samples for dissolved gas analysis. Where volatile or organic compounds are being sampled, inert containers should be used to avoid contamination of the sample.

Water quality data are a vital tool in the monitoring and management of groundwater resources and should therefore be collected and analysed with the utmost attention paid to the nature and origin of the sample. Storage of these data, which can be very expensive to collect, should also be treated as a priority in order to build up a reliable and extensive database on which future aquifer management decisions can be made.
REFERENCES


DRISCOLL, F.G. 1986. Groundwater and wells. 2nd Ed. (Minnesota: Johnson Division).


APPENDIX 1

Summary of sample containers and storage conditions for waters and effluents
(Note: The use of mercury compounds as preservatives is not recommended)

<table>
<thead>
<tr>
<th>Determinand</th>
<th>Container (a) (P = polyethylene, G = borosilicate glass)</th>
<th>Storage Conditions (b)</th>
<th>Recommended max. storage times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity</td>
<td>G</td>
<td>Fill bottle to leave no air space. Store in cool, dark place. (q)</td>
<td>24 h</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>G</td>
<td>Fill bottle to leave no air space. Store in cool, dark place. (q)</td>
<td>24 h</td>
</tr>
<tr>
<td>Aluminium</td>
<td>P</td>
<td>Add 20 ml 5M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Ammonia</td>
<td></td>
<td>See nitrogen.</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>P or G</td>
<td>Add 2 ml 6M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Biochemical oxygen demand (c)</td>
<td>G</td>
<td>Fill bottle to leave no air space. Store at 4°C in dark. (q) (r) (s)</td>
<td>24 h</td>
</tr>
<tr>
<td>Boron</td>
<td>P or soda glass</td>
<td>No special conditions needed.</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>P or G</td>
<td>Store at 4°C out of direct sunlight. (t)</td>
<td>24 h</td>
</tr>
<tr>
<td>Cadmium</td>
<td>P</td>
<td>Add 2 ml 10M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Calcium</td>
<td>P</td>
<td>Add 2 ml 5M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Carbon dioxide free (c) (o)</td>
<td>G</td>
<td>Analyze on site or fill bottle to leave no air space. Store at a temperature lower than that of the sample initially. (q) (s)</td>
<td>&lt;24 h</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>G</td>
<td>Store at 2 – 5°C or add H₂SO₄ to give a pH of 1 – 2. (n) If “dissolved” COD is required, filter before storage. (d)</td>
<td>7 d</td>
</tr>
<tr>
<td>Chloride</td>
<td>P or G</td>
<td>No special conditions needed.</td>
<td>7 d</td>
</tr>
<tr>
<td>Chlorinated hydrocarbons</td>
<td>G</td>
<td>See note (e).</td>
<td></td>
</tr>
<tr>
<td>Chlorine</td>
<td>G</td>
<td>Analyze immediately after sampling.</td>
<td></td>
</tr>
<tr>
<td>- combined (c) (o)</td>
<td>G</td>
<td>Analyze immediately after sampling</td>
<td></td>
</tr>
<tr>
<td>- free (c) (o)</td>
<td>G</td>
<td>See note (e).</td>
<td></td>
</tr>
<tr>
<td>- total organic</td>
<td>G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>P</td>
<td>By AAS - 2 ml/litre of sample. 50% (V/V) HCl by spectrophotometry - 2 ml/litre of sample. 30% (V/V) diluted HNO₃ (d₂₀ 1.42).</td>
<td>6 m</td>
</tr>
<tr>
<td>Cobalt</td>
<td>P</td>
<td>Add 2 ml 50% (V/V) HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Colour</td>
<td>G</td>
<td>Store in cool, dark place.</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Conductivity electrical</td>
<td>P</td>
<td>Fill bottle to leave no air space. Store at 4°C. (q) (r)</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Copper</td>
<td>P</td>
<td>Either 2 ml 50% (V/V) HCl/litre of sample or 1 ml HNO₃ (d₂₀ 1.42)/litre.</td>
<td>6 m</td>
</tr>
<tr>
<td>Cyanide (o)</td>
<td>P or G</td>
<td>Add NaOH to give a pH &gt;12. Store in dark at 4°C. If oxidizing agents are present, it may be useful to add ascorbic acid. (n) (r)</td>
<td>24 h</td>
</tr>
<tr>
<td>Detergents</td>
<td>P or G</td>
<td>Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C. (r)</td>
<td></td>
</tr>
<tr>
<td>- anionic</td>
<td>P or G</td>
<td>Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C. (r)</td>
<td></td>
</tr>
<tr>
<td>- cationic</td>
<td>P or G</td>
<td>Add 40% (V/V) formaldehyde solution to give a final concentration of 1% (V/V). (n) Store at 4°C. (r)</td>
<td></td>
</tr>
<tr>
<td>- non-ionic</td>
<td>P or G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved oxygen (c) (o)</td>
<td>G</td>
<td>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)</td>
<td>24 h</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>P</td>
<td>Fill bottle to leave no air space. Store at 4°C. (c) (r)</td>
<td>24 h</td>
</tr>
<tr>
<td>Determinand</td>
<td>Container (a)</td>
<td>Storage Conditions (b)</td>
<td>Recommended max. storage times</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>---------------</td>
<td>---------------------------------------------------------------------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Free carbon dioxide (c) (o)</td>
<td>G</td>
<td>Analyze on site or fill bottle to leave no air space. Store at a temperature lower than that of the sample initially. (q) (s)</td>
<td>&lt;24 h</td>
</tr>
<tr>
<td>Greases and oil</td>
<td>G</td>
<td>See note (q).</td>
<td>24 h</td>
</tr>
<tr>
<td>Hardness (Total by EDTA)</td>
<td>P or G</td>
<td>No special precautions.</td>
<td>6 m</td>
</tr>
<tr>
<td>Hydrocarbons (o)</td>
<td>G</td>
<td>See note (e).</td>
<td></td>
</tr>
<tr>
<td>Iodide</td>
<td>P or G</td>
<td>Store at 4°C out of direct sunlight. (r)</td>
<td>24 h</td>
</tr>
<tr>
<td>Iron (o)</td>
<td>P</td>
<td>Add 20 ml 5M HCl/litre of sample. (t)</td>
<td>6 m</td>
</tr>
<tr>
<td>* Isotopes (O H)</td>
<td>G</td>
<td>Fill bottles</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>P</td>
<td>Add 2 ml 5M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Lithium</td>
<td>P or G</td>
<td>No special conditions needed. (f)</td>
<td>6 m</td>
</tr>
<tr>
<td>Magnesium</td>
<td>P</td>
<td>Add 2 ml 5M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Manganese</td>
<td>P</td>
<td>Add 20 ml 5M HCl/litre of sample.</td>
<td>6 m</td>
</tr>
<tr>
<td>Mercury</td>
<td>G</td>
<td>Add 20 ml 4.5M H₂SO₄/litre of sample.</td>
<td>38d</td>
</tr>
<tr>
<td>– saline samples</td>
<td></td>
<td>Add HNO₃ to give a pH of 1, and sufficient K₂Cr₂O₇ to maintain excess until analysis starts. (n)</td>
<td></td>
</tr>
<tr>
<td>– non-saline samples</td>
<td>G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals (g)</td>
<td>P (m)</td>
<td>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 HNO₃/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).</td>
<td>6 m</td>
</tr>
<tr>
<td>– total filtrable</td>
<td>P</td>
<td>Filter on site (d) and add 2-10 ml HNO₃/litre of filtrate.</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>P</td>
<td>2 ml/litre of sample 50% (V/V) HCl.</td>
<td>6 m</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>P or G</td>
<td>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 H₂SO₄ to give a pH of 2. (n) Store at 4°C. (q) (r)</td>
<td>24 h</td>
</tr>
<tr>
<td>– hydroxylamine (c) (o)</td>
<td>P or G</td>
<td>Fill the bottle to leave no air space. Store at 4°C. (q) (f) (s)</td>
<td></td>
</tr>
<tr>
<td>– hydrazine (c) (o)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– kjeldahl (c) (o)</td>
<td>P or G</td>
<td>Unless free ammoniacal nitrogen is also required add H₂SO₄ to give a pH of 2. (n)</td>
<td>24 hrs</td>
</tr>
<tr>
<td>– nitrate (c)</td>
<td>P or G</td>
<td>Store at 4°C. (r)</td>
<td></td>
</tr>
<tr>
<td>– nitrite (c)</td>
<td>P or G</td>
<td>Store at 4°C. (r)</td>
<td>24 h (6 m if acid)</td>
</tr>
<tr>
<td>– organic (c) (o)</td>
<td>P or G</td>
<td>Unless free ammoniacal nitrogen is also required add H₂SO₄ to give a pH of 2. (n)</td>
<td>48 h</td>
</tr>
<tr>
<td>Odour (c)</td>
<td>G</td>
<td>Store at 1 – 5°C. (q) (r)</td>
<td>24 h</td>
</tr>
<tr>
<td>Oils and greases</td>
<td>G</td>
<td>See note (e).</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Organic carbon total</td>
<td>G</td>
<td>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)</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Organic chlorine total</td>
<td>TOX</td>
<td>See note (e).</td>
<td>5d</td>
</tr>
<tr>
<td>Determinand</td>
<td>Container (a)</td>
<td>Storage Conditions (b)</td>
<td>Recommended max. storage times</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------</td>
<td>--------------------------------------------------------------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Organo-phosphorus pesticides</td>
<td>G</td>
<td>Immediately after sampling, add solvent to sample, shake, and store in spark-proof refrigerator at 4°C. (n)(r)</td>
<td></td>
</tr>
<tr>
<td>Oxygen demand</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– biochemical (c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– chemical</td>
<td>G</td>
<td>Fill bottle to leave no air space. Store at 4°C in the dark. (q) (r) (s)</td>
<td>24 h</td>
</tr>
<tr>
<td>– total</td>
<td>G</td>
<td>Store at 2 – 6°C or add H₂SO₄ to give a pH of 1 – 2. If dissolved COD is required, filter before storage. (d) (n) (r)</td>
<td>7d</td>
</tr>
<tr>
<td>Oxygen dissolved (c) (o)</td>
<td>G</td>
<td>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)</td>
<td>24 h</td>
</tr>
<tr>
<td>Permanganate value</td>
<td>G</td>
<td>Add H₂SO₄ to give a pH&lt;2. (n)</td>
<td></td>
</tr>
<tr>
<td>Pesticides organo-chlorine</td>
<td>G</td>
<td>Store at 4°C. (r)</td>
<td>&lt; 24 h</td>
</tr>
<tr>
<td>* Phenols</td>
<td>G</td>
<td>4°C/H₂PO₄ to pH &lt;4</td>
<td>24 h</td>
</tr>
<tr>
<td>* Potassium</td>
<td>P</td>
<td>Add HCl to pH &lt;2</td>
<td>6 m</td>
</tr>
<tr>
<td>* Silica</td>
<td>P</td>
<td>Filter, plastic container</td>
<td>6 m</td>
</tr>
<tr>
<td>Sodium</td>
<td>P</td>
<td>No special conditions needed</td>
<td>6 m</td>
</tr>
<tr>
<td>Sulphate</td>
<td>P or G</td>
<td>Store at 4°C. (If sulphide and/or sulphite present, fill bottle to leave no air space). (q) (r)</td>
<td>7d (6m if acid)</td>
</tr>
<tr>
<td>Sulphide (o)</td>
<td>P or G</td>
<td>Fix sample by adding zinc acetate and sodium hydroxide reagents on site. (n)</td>
<td></td>
</tr>
<tr>
<td>Sulphite (o)</td>
<td>P or G</td>
<td>Fill bottle to leave no air space. Store at 4°C. (r) (s)</td>
<td>24 h</td>
</tr>
<tr>
<td>Solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>– dissolved</td>
<td>G</td>
<td>No special conditions needed</td>
<td></td>
</tr>
<tr>
<td>– separable</td>
<td>G</td>
<td>No generally-suitable procedure. Analyze as soon as possible.</td>
<td></td>
</tr>
<tr>
<td>– suspended (c)</td>
<td>G</td>
<td>No generally-suitable procedure. Analyze as soon as possible.</td>
<td></td>
</tr>
<tr>
<td>– total</td>
<td>G</td>
<td>Store at 4°C. (r)</td>
<td></td>
</tr>
<tr>
<td>Turbidity (c)</td>
<td>G</td>
<td>No generally-suitable procedure. Analyze as soon as possible.</td>
<td>7d</td>
</tr>
<tr>
<td>Zine</td>
<td>P (m)</td>
<td>Either 7 ml/litre of sample 50% (v/v) HCl or 1 ml/litre of sample HNO₃ (d 1.42)</td>
<td>6 m</td>
</tr>
</tbody>
</table>
Notes:

(a) For precautions relevant to the choice and use of containers, see Sections 4.7, 4.8.3, and 4.9.2.

(b) It is essential to ensure that the storage conditions selected, including the use of cooling, do not adversely affect the performance of the analytical method.

(c) These determinands are often particularly liable to instability, and it will often be important to take special steps to minimise the time between sampling and analysis.

(d) For precautions relevant to the choice and use of filters and filtration equipment, see Sections 4.8.4 and 4.9.2.

(e) These determinands cover such a large number of compounds with such a wide range of properties that only general points concerning preservation are made here, and individual analytical methods should be consulted for detailed information. In general, storage of samples in the dark at 4°C is desirable, and bottles should be completely filled when volatile substances are of interest. Certain determinands may require the addition of preserving reagents; for example to preserve haloforms, sodium thiosulphate may need to be added to destroy chlorine. (See note (n)). Analyze as soon as possible, preferably within 24 hours.

(f) Contamination of samples by lithium leached from polyethylene bottles has been reported (99).

(g) The term "Metals" includes the following: Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Sr, Sn, U, V and Zn. The container and method of preservation quoted in the table are thought to be generally useful for this group of metals. However, other preservation procedures may also be satisfactory. When other procedures are given in analytical methods for metals in the above group published by the Standing Committee of Analysts, these have been included under the individual metals in the table.

(h) Only the two most common determinands concerning phosphorus are included. Many different fractions of phosphorus may be distinguished, and may also require particular preservation procedures. Reference should be made to the analytical methods for appropriate details.

(k) Where no reference is given, the information was supplied by members of the appropriate SCA Working Groups (3, 4, 5, 6, 7, 8 and 9). For detailed information see the appropriate booklets in this series. Note that much sampling and sample storage information is also contained in the Essay Review Booklets in this series on analytical techniques.

(l) The reference only refers to the use of nitric acid.

(m) Contamination of samples by zinc and other metals leached from plastics has been reported. If in doubt check bottles using distilled water and the desired preservative before use. Discard unsuitable bottles.

(n) If not negligible, note the volume of preservative added or the resultant volume change.

(o) Aerate the sample as little as possible during the filling of the sample bottle.

(p) See also Reference 187.

(q) If no air space is left in a glass bottle, care should be taken to prevent the bottle heating and so generating enough pressure that it bursts.

(r) Care should be taken to prevent accidental freezing in glass bottles.

(s) See Section 4.7 iia.

(t) If iron II or manganese II, or other easily oxidized metals in lower oxidation states are to be determined by oxidation state rather than as total metal, it may be necessary to completely fill bottles (see notes (q), (r) and (s)). For some highly reactive waters the bottles may need to be filled with inert gas prior to sampling to avoid oxidation during filling.

This table is duplicated from SCA, 1980, with determinands of special interest to groundwater investigations added. Maximum recommended storage times have been added from Scalf et al. (1981) and Barcelona et al. (1985). All Sections and References mentioned in these notes refer to SCA, 1980.