GROUNDWATER SAMPLING MANUAL

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GROUNDWATER SAMPLING MANUAL

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Gezina 0031

Orders@wrc.org.za **or download from www.wrc.org.za**

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Project Team

Project Leader: Dr M Gomo

Principal Researchers: Mr F de Lange and Prof Danie Vermeulen

MSc Geohydrology students: Ms TB Molokwe, Ms EG Bredekamp and Ms Malefa Moleme

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

CHAPTER 1 BACKGROUND INFORMATION

There is no best single method that will suit all sampling objectives/needs or is applicable at all sites or times. Thus, as new methods, techniques and equipment are developed, there is need to continuously update the groundwater sampling manual (GSM) in line with the state-of-the-art to provide best practice guideline. In some other instances, new groundwater sampling needs might arise and such will also require updating of the existing sampling guides.

This guide presents an update version of the 2nd edition of the WRC's Groundwater Sampling Manual (Weaver, Cave, and Siep 2002). The 1st edition of the manual was developed by Weaver (1997). The current groundwater sampling guide emanates from a WRC-funded project (Project no. 2428). The project was entitled "Update of the Groundwater Sampling Manual". The sampling manual has been updated to include guide about:

- Factors that can contribute to sample bias and measures to reduce or eliminate sample bias,
- Use of the Fluid Electrical Conductivity (FEC) profiling as a basic technique to locate groundwater flow zones that can be targeted for sampling,
- Passive sampling devices,
- Use of a stainless flow-through bailer as a passive sampling method,
- Decontamination procedures for different determinants,
- Sample preparation, preservation procedures, storage and holding times for different determinants,
- Direct push technology (DPT) as an emerging sampling approach,
- Sampling of deep boreholes,
- Sampling of dissolved gases (DG) in groundwater and
- Evaluation of uncertainties associated with the sampling process and analysis of groundwater samples as part of quality assessment (QA).

It is important to highlight that not all aspects added in this revised sampling manual are new. Some of these aspects have been there for decades, and their inclusion is based on the existing needs raised by groundwater professions during an investigative survey conducted at the onset of the project. In this sampling manual, other aspects have been restructured in their presentation and layout for the previous guides (1st and 2nd Editions) to improve the user-friendliness of the manual. The manual makes use of decision tree diagrams to guide users on which tool to apply, when and how to collect the representative results while reducing the sampling cost. The choice of sampling the method/procedure should always be driven by the goal of sampling.

1.1 Purpose

The purpose of the groundwater sampling manual the same as the previous editions, and that is to provide guidance on consistent groundwater sampling techniques that will ensure that all groundwater quality data collected is representative of in-situ groundwater quality at the time of sampling. Using these guidelines will reduce sampling errors thereby improving the quality of the data. Groundwater quality data collected according to these described techniques can then *reliably* be used to evaluate hydrogeochemical conditions.

This manual does not pretend to be exhaustive and provide all the answers to all groundwater sampling needs or requirements. What this manual does provide, however, is sufficient technical detail for hydrogeologists involved in *water-supply projects* to collect groundwater samples using appropriate methods, and to conduct hydrogeochemical investigations of natural systems. At the same time, the manual provides fundamental base for the majority of groundwater pollution investigations. However, for highly complex groundwater pollution projects, the groundwater practitioner will have to look for specific and up-to-date sampling guidance on pollutants of interest. The bulk of published information used for this manual is derived from the developed countries, in particular Australia, Canada, UK and USA. It will be very difficult to list all useful references. However, most of the information can be accessed through Google searches.

It is not the intention of this guideline to discuss aspects of hydrogeological/geohydrological assessments in any detail. The sampling guide assumes that trained groundwater practitioners understand how to design groundwater monitoring networks for different needs and hydrogeological conditions. Furthermore, the practitioner must know how the boreholes/piezometers should be drilled or installed, constructed and developed for the purposes of groundwater monitoring in line with local standards and in some cases international standards.

The manual does also not describe in any detail the behaviour of determinants in the sub-surface, or any such hydrogeochemical processes nor are there any descriptions of laboratory analytical methods.

1.2 Limitations

This manual is mostly developed based on the information that has been synthesised from literature review from reports of the work that has been conducted in mostly developed countries. For comprehensive understanding readers often referred to cited sources whose references are listed at the end of section.

1.3 National guidelines and standards

The sampling manual is not meant to replace specialised sampling protocols or any other regulatory standards and guidelines. It is therefore important to consult the national standards and guidelines in use in relation to your specific project. The manual only serves to provide guidance for groundwater sampling based on the best practices to support the existing national standards and guidelines. Some of the national guidelines and standards related to groundwater sampling, monitoring and water quality assessments include:

- Department of Water Affairs and Forestry (2006). Best Practice Guideline – G3: Water Monitoring Systems Series G: General Guidelines. Pretoria, South Africa
- DWAF (1997) Minimum Standards and Guidelines for Groundwater Resource Development for the Community Water Supply and Sanitation Programme. Department of Water Affairs and Forestry. Pretoria, South Africa
- SANS 10299-2:2003. Development, maintenance and management of groundwater resources Part 2: The design, construction and drilling of boreholes. Standards South Africa. Pretoria, South Africa.
- SANS 5667-11:2015/ ISO 5667-11:2009. Water quality – Sampling – Part 11: Guidance on sampling of groundwater. Standards South Africa. Pretoria, South Africa.
- SANS 241-2:2015. Drinking water Part 2: Application of SANS 241-1. SABS Standards Division. Pretoria, South Africa.

1.4 Layout of the manual

The GSM consist of three main phases; pre-sampling, sampling and post-sampling (Figure 1). The chapter on sampling of springs, seeps, pits and hand-dug boreholes is brought from the previous manual (Weaver et al. 2007).

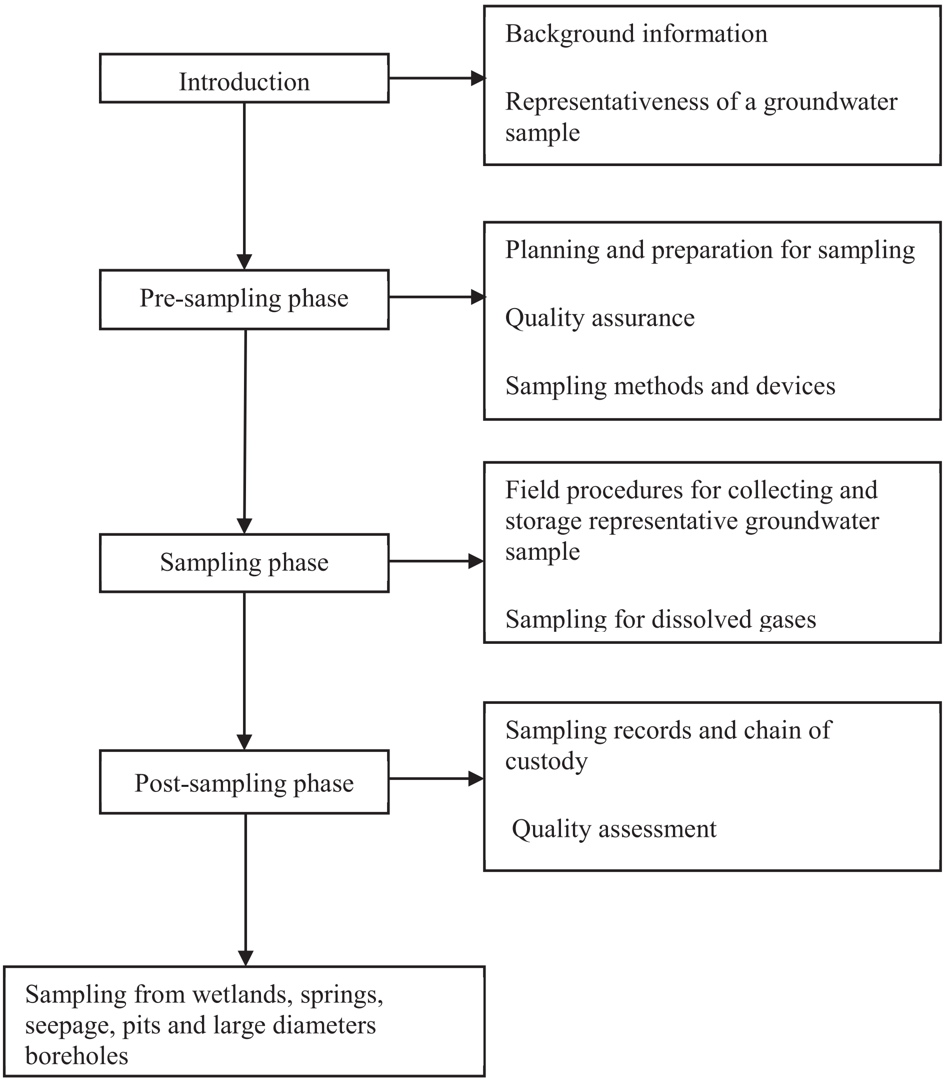


Figure 1 Flow diagram showing the layout of the sampling manual

CHAPTER 2 REPRESENTATIVENESS OF A GROUNDWATER SAMPLE

2.1 What constitutes a representative groundwater sample?

The objective of any groundwater sampling programme and plan is to collect representative groundwater. A representative groundwater sample must reflect the in-situ chemical and microbial status of the groundwater at the *time* of sampling and *location* of sampling within the aquifer (CL: AIRE 2008). However, what constitutes a representative groundwater sample can be relative depending on the objective of sampling. The objective of sampling is defined in the groundwater sampling programme and these take into consideration project goals. The representativeness of a groundwater sample should therefore be defined during the design and development of a sampling programme as part of the data quality objectives (DQO). DQO define the target in terms of the quality of the data expected and specification of tolerable or acceptable limits appropriate for the purposes of groundwater monitoring goals.

CL: AIRE (2008) provides a detailed description and explanation on defining the representativeness of a groundwater sample for two typical cases on groundwater pollution assessment and quality investigation. Table 1 gives a summary of the basic aspects to consider when defining the representative of a groundwater sample for groundwater pollution assessment and quality evaluation.

Table 1 Basic aspects to consider when defining the representativeness of a groundwater sample for groundwater pollution assessment and quality evaluation

Groundwater pollution assessments	Groundwater quality evaluation
Target of depth-discrete groundwater flow zones	Volume-averaged groundwater chemistry
Precise location of discrete groundwater flow zones	
Short screens installed	Monitoring boreholes equipped with long screens to obtain composite samples (mixed and sometimes diluted)
Precise location and sampling of contaminant distribution	
Precise location and sampling of peak (undiluted) contaminant concentration	

Source: CL: AIRE (2008)

The representativeness of a groundwater sample will to a large extent depend on how the sample is collected. During the groundwater sampling process, a wider range of factors can positively or negatively influence the sample representativeness resulting in sample bias.

2.2 Sample bias

Sample bias is a measure of the difference between the analysed and true groundwater sample chemical and microbial composition that is supposed to be obtained under in-situ aquifer conditions at the particular *time* and *location* of sampling. This difference can either be positive or negative, and is generally referred to as the sampling error. While the objective is always to minimise the sampling error, this task is compounded by the fact that the true in-situ groundwater composition is actually never known. The principle of operation is that by collecting, preparing and handing samples using scientifically proven methods and procedures the sampling errors can be reduced to a minimum. Sampling errors result from the influence of both systematic and random errors. Systematic errors are introduced by an inaccuracy of observation or measurement inherent in the system and result in consistent and reproducible bias in sampling data (Keith 1991). Random sampling errors are those due to random and unpredictable factors leading to inconsistent and non-reproducible bias in sampling data irrespective of the accuracy (Keith 1991; Nielsen and Nielsen 2006). Table 2 shows the main causes of systematic and random errors.

Table 2 Main causes of systematic and random errors

Systematic errors*	Random errors**
Inappropriate borehole designs (construction and development)	On-site contamination of aqueous samples with solid matter or residue
Inappropriate sampling equipment	Contamination from sampling equipment (depends on equipment handling, cleaning and decontamination)
Inappropriate sampling preparation, handling and storage	Cross contamination due to sample carry-over from the previous sample

Sources: Nielsen and Nielsen 2006, Environmental Agency (2002)***

The meaning of the analysed composition of a groundwater sample is always related to *time* and *location* of sampling point. Groundwater chemical and microbial composition is influenced by various factors and processes which are all subject to change with time and space. While the time of sampling can be varied as defined by sampling frequency, the location of a sample in the aquifer is fixed by virtue of the position of the sampling borehole that is decided during the designing of monitoring network as part of groundwater sampling programme.

2.3 Sources of sample bias

It is important to identify, understand and describe all the potential sources of sample bias during the development of sampling programme. These potential sources of bias have to be documented, including their corrective actions where possible before the onset of the sampling process.

Drilling, construction and development of monitoring boreholes

Groundwater samples are mainly collected through borehole or piezometers, thus drilling, construction and development processes have an important influence on the collected sample. If the drilling, construction and development is not appropriately done, it can greatly contribute to the sample bias thereby affecting the representativeness of a collected sample. Detailed aspects on borehole drilling, construction and development are comprehensively addressed in a number of sources (Driscoll 1986; Nielsen 1991). These should be consulted to improve understanding of these processes. A summary of the potential influence of drilling and construction on the sample bias is provided in Table 3 (Adopted from the guide of EPA Australia 2000).

Table 3 Potential influence of drilling and construction on the sample bias

Installation stage	Main potential effect/influence
Drilling technique	- Disturbs the aquifer formation through smearing (e.g. rotary auger) and compaction (e.g. cable tool) of borehole walls, - Can cause transport of geological formation materials and drilling fluids into different zones, and - Might clog groundwater flow path, thereby restricting pollution from the monitoring hole
Drilling fluids (Include: air, water and specific drilling mud formulations or native clays)	- Air may cause oxidation and precipitation of analytes of interest, - In highly permeable formations, air may also cause severe disturbance of hydrochemical profiles, - Drilling water may dilute or flush groundwater near the borehole, modifying the chemistry, - Drilling water may also cause precipitation of minerals, thereby blocking contaminant and groundwater flow pathways, - Mud may clog preferential groundwater pathways, or clay particles within mud may sorb some electrically charged contaminants, and - Drilling mud additives such can bring physical and chemical changes – the chemicals are typically hydrocarbons based and their degradation could affect the microbial quality of the groundwater.

Borehole construction (Screen material, design and placement of borehole screens)	- Incompatible casing and screen material may result in either leaching or sorption of analytes of interest, - Desorption of analytes of interest might occur should water quality change, - Diffusion of organics may also occur through polymeric casing materials, - Short screens placed on groundwater flow zones are ideal, long screens can result in a composite sample through mixing, - Poorly placed screens may fail to intercept these zones,
Gravel packs or annular fills	- Materials used should be inert, otherwise can alter the chemistry
Location of sampling depth	- Inappropriate location of depth, results in wrong sample,
Borehole development	- Poor development limits the hydraulic connection between the bore and the formation, thereby affecting replenishment, and - Poor development increases turbidity due to high suspended solids thereby brining the need to filtering and its potential consequences.

Source: Adopted from the guide of EPA Australia (2000)

Examination and assessment of the monitoring borehole

- *Examine and assess the conditions of groundwater monitoring boreholes to ensure that they will enable sampling programme objectives to be met,*
- *This requires comprehensive examination of monitoring borehole drilling, construction, development and screen location details and an inspection of the borehole to establish its physical condition,*
- *Borehole cameras can also be used to reveal the inside of a borehole, and*
- *Make use of the local guidelines/standards on borehole construction as much as possible.*

Sampling and sample analysis

During the sampling and analysis processes there is a variety of factors that does contribute to sample bias. However, their contribution to the sample bias is only evaluated after the sampling and analytical process as part of the quality control through uncertainty analysis (*POST-SAMPLING PHASE*).

References

CL: AIRE (2008). Principles and practice for the collection of representative groundwater samples. Technical Bulletin (TB) 3. Contaminated land: Applications in Real Environment (CL: AIRE).

Driscoll FG (1986). Groundwater and Boreholes, 2nd Edition, Johnson Division, St. Paul, Minnesota

Environmental Agency (2002). Guidance on the monitoring of landfill leachate, groundwater and surface water, TGNO2.

EPA Australia (2000). Groundwater Sampling Guidelines. Southbank Victoria, Australia.

Nielsen DM (1991). *Practical Handbook of Groundwater Monitoring*, Lewis Publishers, New York.

Nielsen DM and Nielsen GL (2006). Groundwater Sampling. In Practical handbook of environmental site characterisation and groundwater monitoring, edited by Nielsen DM. CRC-Taylor & Francis, 2nd Edition, 959-1112.

PRE-SAMPLING PHASE

CHAPTER 3 PLANNING AND PREPARATION

3.1 Groundwater sampling programme

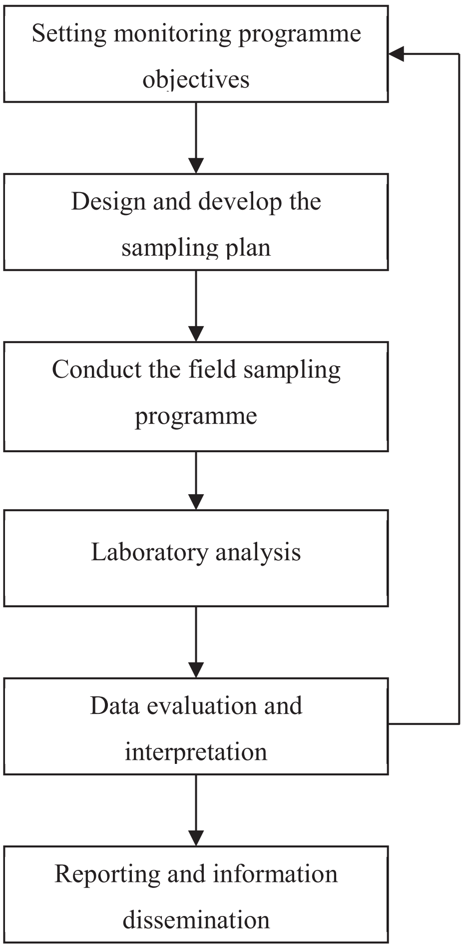
A groundwater sampling programme provides detailed description of the procedures used to collect, handle and analyse groundwater samples in order to achieve groundwater monitoring goals. The sampling programme is prepared prior to sampling in line with groundwater monitoring goals, and takes into account site specific history, hydrogeological and hydrogeochemical characteristics. An example of the necessary site-specific background information required in order to develop a sampling programme is given in Table 4 (EPA Australia 2000).

Table 4 Site specific background information required in order to develop a sampling program

Site history	Hydrogeological setting	From previous filed investigation
Contaminants of concern; potential for groundwater contamination at the site; for example, contaminant use, past practices and incident history	Aquifer type and configuration	Borehole (lithology logs) and water level measurements
	Groundwater flow directions and rates	Depth and construction details
	Vulnerability of the aquifer system to contamination	Depth and length of screened interval

Source: EPA Australia (2000)

Groundwater sampling is part of monitoring programme. The framework for a water quality monitoring programme (Figure 2) is comprehensively discussed by ANZECC (2000). The processes involved are interactive and iterative in order to ensure that the objectives of the programme are kept in mind and the programme can be reassessed if necessary. The objectives should never be cast in stone. Conversely, the monitoring programme should only be altered if there is a real and valid reason and the change will result in a better end result. This groundwater sampling manual is not intended to describe in any fine detail the development of a monitoring programme. It is rather a description of the methods within the part of the programme that is described as “field sampling methods”.



Source: (modified from ANZECC 2000)

Figure 2 Framework for a water quality monitoring program

3.2 Sampling plan

A sampling plan provides specific details of the sampling methods, procedures, equipment and devices important to execute the sampling process. Development of a sampling plan is the first step of any groundwater sampling exercise/event. The plan should therefore provide sufficient description of:

- Why sampling?
- What to sample?
- How to sample it?
- Where to sample?
- When to sample?
- Who should sample?

It is also important to *identify* a suitable analytical laboratory and also to discuss with them and understand their sample requirements and quality of analysis.

Answers to the questions in Table 5 will also help you to compile a checklist of items, equipment and devices needed to plan and prepare for the groundwater sampling exercise (Waterwatch 2005).

Table 5 List of questions that will help to develop a sampling plan and compile a checklist of field requirements

Monitoring objectives	• Why do you have to sample groundwater? • What are you going to sample?
Data quality objectives	• Who will use or evaluate your data? • How will the data be used or evaluated? • What is the level of data quality is required data quality objectives? • What are requirements and quality of analytical laboratory? • How will you ensure your data is scientifically credible? • How will the data be managed and reported?
Sampling process	• What methods will you use to collect the sample? • What kind of sampling containers are needed and how many? • What equipment and devices do you need to collect the sample? • How will the sample be preserved, stored and shipped? • Where will you sample? • Who will be involved in the sampling process? • What is the sampling frequency? • Is there any regulatory sampling guide or requirements?
Site hazards	• What potential hazards are there associated with the sampling? • How can these hazards be mitigated?

Source: (Waterwatch 2005)

3.3 Quality assurance (QA) planning

Quality assurance (QA) is a set of operating principles, procedures and actions which, if strictly followed during sample collection and analysis, will produce data of known, consistent and defensible quality. That is, the accuracy of the analytical result can be stated with a high level of confidence. Included in quality assurance are quality control and quality assessment aspects. When the QA is good and correct, the analytical results cannot be rejected as being invalid by a court of law.

Quality assurance is implemented from the design of sampling the program right to the delivery of the sample at the laboratory. Remember that sampling can be one of the most error-prone sections of any monitoring programme. Certain controls are necessary to ensure that sampling is conducted as consistently as possible. Analytical results are only as good as the samples they are testing. Keith and Wilson (1982) suggest the format and a list of aspects that should be included in a QA plan (Table 6).

Table 6 Suggested format and a list of aspects that should be included in a QA plan

Sections	Contents
Format (A)	Title page and table of contents
Project overview – what is the purpose of the project? (B)	Project description, project organisation and responsibility
Data quality objectives – what will be required? (C)	QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability
Measurement activities – how will it be done? (D)	Sampling procedures; Sample custody; Calibration procedures and frequency; Analytical procedures; Data reduction, validation, and reporting; Internal quality control checks and frequency; Preventive maintenance
Quality assurance – can the results be trusted? (E)	Performance and systems audits and frequency; Specific routine procedures to be used to assess data precision, accuracy and completeness of specific measurement parameters involved; Corrective action and quality assurance reports to management.

Source: Keith and Wilson (1982)

This grouping could be useful in at least a couple of ways. For someone writing a QA plan, particularly for the first time, it might clarify the way in which the different items relate to each and to the plan as a whole. Additionally, there are occasions, particularly in small or short-term projects, when something less than a complete QA plan would be appropriate. In these cases, a smaller document organised around the major headings listed above might be in order.

3.4 Quality control (QC)

In groundwater sampling, quality control provides a detailed set of procedures intended to ensure that the sampling process is performed accordingly and adheres to a defined set of procedures and that it meets the requirements of the sampling programme to achieve the DQO. The QC process is therefore is designed to verify the performance characteristics of the whole sampling process. The following internal field QC control methods should be followed.

Blanks

Blank samples provide the basis to assess the influence of potential contamination on the samples. Potential sources of contamination assessed include; cleanliness of the bottles, preservative purity, efficiency of equipment decontamination, environmental conditions, storage and transportation of samples.

1. Full Trip Blank (FTB)

A **trip blank** is prepared before going to the sampling trip and carried throughout the trip. Identical bottle to the ones used for sampling is filled with deionised water. The bottle is carried in the stored, transported and handled in the same way with the samples. It is returned to the laboratory with the samples and is analysed at the same time as the field samples. The FTB assesses the potential influence of external factors during the whole process and trip on the analysed samples, more important VOCs and dissolved gases. If sampling is done over more than one day, then it’s best to take a FTB for each day’s samples.

2. Field Transfer Blanks (FXR)

This is done for VOCs and perhaps dissolved gases. Fill the preserved volatile organic analysis (VOA) sample bottles at the sampling point with reagent or deionised water that has been transported to the field. This is used to evaluate potential contamination due to field conditions. Prepare, store, handle and transport the FXR bottles under the same conditions with the rest of the samples

3. Equipment blanks

This is needed to assess the efficiency of the decontamination process. When the same sampling pump is used for several pollution monitoring boreholes, collect an equipment blank (also known as a field blank). Choose one of the boreholes showing the highest level of contamination, decontaminate the sampling equipment, and pass through deionised water then collect a sample of the equipment blank. Alternatively, two samples can also be collected; one before decontamination and one after decontamination, analysis from the two samples are compared to assess the efficiency of the decontamination process.

Duplicate samples

These samples are used to assess the precision of measurement of the analytical laboratories. Send a duplicate sample with the set of samples to the laboratory. Collect twice as much sample from the same borehole, and split into two different bottles. Label these bottles differently. Make sure they are recorded correctly on the sample record sheet. A second set of duplicates can be sent to another laboratory for quality assurance (external quality control). These samples must be preserved, filtered, stored and transported like any the rest of the samples.

To collect duplicates Sundaram (2009) recommends that once in every 10-15 monitoring boreholes, triplicate samples should be taken to provide the following set of samples; original; split duplicates and spiked samples.

1. **Original** – sample is the actual sample collected from the borehole,
2. **Split duplicates –** one sample is split into 3 subsamples or each is given its own identification number, and
3. **Spiked duplicates** – known concentrations of a number of elements are added to a sample. Spiking solutions are transported with the field and then added into the duplicate sample (See Sundaram 2009 for specific details).

3.5 Field equipment list

The following items may be of use for field sampling of groundwater (Table 7). Use this list to make your own list that is specific for the project or sampling site. Add the equipment lists for specific field measurements as described in the various sections of the manual. Pack equipment in the vehicle taking into consideration the order in which it will be required. A basic list of field equipment and devices required for a sampling event or exercise is shown in Table 7.

> **Before packing the equipment**, *calibrate all the field measuring equipment and ensure that it is in working order.*

Table 7 A list of field equipment required for the sampling event or exercise

Borehole location	Borehole operation
1. Map or instructions for locating the sampling site or sites 2. Letter of introduction and visiting cards 3. Key to get into site and lubricant for padlocks 4. Global Positioning System	1. Water level recorder, tap water to clean recorder, spare batteries 2. Tape measure (as long as possible) 3. Pump or purging device, power, compressor 4. Downhole logging equipment 5. Clear plastic bailer, if you expect NAPL 6. Containers for purged water and to measure pumping rate 7. Sample record sheets to identify sample and/or sample sets and to record field measurements

	8. Shovel, slasher, hammer and etc.
Toolbox	**Field measurements**
1. Torch 2. Indelible ink fibre tip pen/s, pencils, ballpoint, field note book, micro-cassette recorder (especially useful for recording field notes in the rain) and calculator 3. Protective clothing. This includes rain gear, cold weather gear, warm clothing, sunglasses and sun hat. 4. Camera, plus film or memory chip 5. First aid kit (commercially available kits) 6. Drop sheet (some type of sheeting to protect instruments from contamination in the event of their falling to the ground) 7. Folding table or other work surface 8. Personal equipment: money, driver's license, identity card, credit card, food and drink etc. 9. Decontamination kit, sprays, detergent, buckets, soap, rinse water and PVC pipe.	1. Flow-through cell 2. Thermometer, Conductivity meter 3. pH meter, electrode and buffer solutions, thermometer 4. Eh meter, electrode and buffer solution, thermometer 5. Spare batteries for the all meters 6. Dissolved oxygen meter plus reagents 7. Wash bottle (distilled water) 8. Extra distilled water 9. Titration kit for alkalinity/acidity 10. Permanent markers or any other form of labels
Sample collection	
1. Labels and transparent tape to cover them 2. Chain of Custody sheets 3. Sample bottles, caps plus foil and Teflon inserts when necessary. 4. Bottles or ampoules containing preservatives (clearly labelled) and 5. Filter apparatus for field filtered samples, including extra filters 6. Preservation equipment e.g. ice box/cool box with cooling medium such as frozen ice-bricks, ice. Foil to protect those samples sensitive to light 7. Paper towels, rags, plus plastic garbage bags for discards	

3.6 Health and safely

While sampling itself is generally a low hazard type of work, it is the environment and facilities where most of the sites that require groundwater quality assessments monitoring which possess huge threat to health and safely. It is important that a general health and safety plan is developed for each sampling site and also for each sampling exercise. The health and safety plan must therefore be able to:

- Identify the potential hazards associated with sampling and
- Provide detailed and specific procedures and list of actions that will be undertaken to remove or lower the risk.

Health and safety items to have in the list of items for sampling include:

- *Comprehensive first aid kit,*
- *Mobile or satellite phone,*
- *Emergency numbers,*
- *Check out and check in protocol – another person should know when you are out sampling and when you're back,*
- *Fire extinguisher,*
- *Escorting if there's need,*
- *Personal Protective Equipment (PPE), and*
- *Material Safety Data Sheet (MSDS) for every chemical to be involved.*

Common hazards associated with sampling can be generally grouped into two; those directly associated with sampling equipment, sampling medium or analytes of interest and natural ones (Table 8).

Table 8 Examples of some of the hazards associated with sampling

Hazards directly associated with sampling equipment/tools or substances	**Natural hazards**
Physical injuries from the equipment Vehicle breakdown or accident, getting stuck in wet conditions or sand soils Toxic gases such as hydrogen sulphide, VOC vapours Exposure to hazardous substances e.g. decontamination chemicals, analytes, toxic products formed from sample preparation Traffic when working in Urban areas (Use traffic cones and reflectors) Abandoned mines shafts and subsidence	Snakes Wasps and bees Scorpions Watch out for stray wild animals Holes and ditches

The general safety procedures and measures for groundwater sampling at sites are discussed in Sundaram (2009).

General safety procedures and measures

- *On approaching each sampling site or borehole, carefully inspect the general areas to identify any possible hazards,*
- *Also watch out when opening the borehole, there could be wasps, bees or a snake ……….*
- *Determine the location(s) of the nearest healthcare facility(s) to the sampling site or area, important to map out the quickest routes to get there,*
- *Identify and avoid hazards associated with electrical lines or connections, especially if water or wet ground is present in the field,*
- *Pumps that are deployed down a hole should be secured to effectively counter-balance the weight of water-filled tubing down the hole.*
- *Generators should be regularly tested, and earthed to prevent electrical accidents at waterlogged sites. Best to use generators with the automated trip-out device, ensure that the cable connections are protected from moisture and physical damage,*
- *The engines, exhausts, and some pipes close to an operating pump can be extremely hot, do not touch such surfaces,*
- *Ensure that the generator is placed in such a way that the emitted gases doesn't affect people directly,*
- *Exercise extreme caution – be careful with glass acid vials for sample preservation. The acid itself is extremely hazardous and must be washed off skin and/or clothing immediately if the sampler comes into contact with it,*
- *Develop a remedy plan for the expected hazards and*
- *It is best to have at least two sampling personnel at a site, in order to help if the need arises.*

Remember that *for groundwater quality monitoring sites at industrial facilities such as mines, oil and gas also have their own set of safety rules and regulations which must be followed in addition to the ones for sampling. It is therefore prudent to inquire in advance from the site owners about their in-house safety and healthy protocols, and if there is a compulsory healthy and safety induction/training, this information is essential for planning.*

Protective clothing for general sampling

Protective clothing must be sufficient to safeguard the health of the sampler. Education and training of sampling personnel in correct procedural methods is required by law and can prevent accidents. Safety Acts usually stipulate that personnel are made aware of the potential hazards and the need for safety precautions. It is the responsibility of the project leader or manager to ensure that proper safety equipment is made available, that the sampling personnel are trained in the use thereof, and that the safety equipment and use thereof is specified in the Monitoring Program Guide. Examples of basic protective clothing for general sampling include:

- Safety shoes,
- Work suit,
- Grip and latex gloves, and
- Sunhats and sunscreen where applicable.

3.7 Selection of determinants/parameters

The selection of determinants to be analysed depends on the purpose of the groundwater quality survey and monitoring goals and these need careful consideration. However, regulations can also dictate the specific parameters that have to be analysed and monitored for compliance purposes. One must first check if there are any local or internationals regulations. Once the purpose/aim of sampling has been established, see examples in Table 9 to guide you the selection of determinants for analysis. The knowledge and understanding required to select determinants analysed *must* be acquired from the training curriculum of the groundwater practitioner (hydrogeologist/geohydrologist). This manual will only serve as a guide.

Table 9 Detailed sampling tree table to guide the selection of determinants

Aim	Application	Field measurement[1,2]	Determinants to be measured in the laboratory
Water quality for consumption	Household consumption	EC pH	Cat/An[3] Microbiology[4] Iron, Manganese and other elements if a problem is suspected e.g. encrustation/corrosion
	Livestock drinking	EC pH	Sulphate, Fluoride and NO_3 if a problem is suspected
	Irrigation	EC pH	Cat/An, Iron/Manganese, encrustation/corrosion
	Industrial usage	EC pH Eh (Alkalinity)	Cat/An, encrustation/corrosion, Iron/Manganese
Hydrogeochemistry assessments/surveys	Major hydrochemistry	T EC pH Eh	Cat/An plus what project needs
	Trace elements	T EC pH Eh	Cat/An plus trace elements as project needs
	Radioactivity	T EC pH Eh DO (alkalinity)	Determined by project
	Isotopes	T pH DO (alkalinity)	Determined by project
	Artificial recharge	T pH Eh DO	Cat/An, DOC, microbiology, phenols and DOX

Groundwater contamination/pollution investigations	Waste disposal sites	pH Eh DO	Cat/An, DOC, DOX plus toxic substances of interest
	Unconventional oil and gas exploration sites	T EC pH Eh DO (alkalinity)	Cat/An, Volatiles and semi-volatiles DOC, dissolved gases and toxic substance of interest
	Pesticide contamination	pH Eh DO	Identified target pesticides, nitrate and potassium
	Acid mine drainage (AMD)	pH Eh DO	Cat/An, identified trace elements
	Industrial waste pollution	pH Eh DO	Determined by the process
	Sewage disposal	pH Eh DO	Cat/An, DOC, microbiology parameters
	Underground storage tanks (UST)		Volatiles and semi-volatiles DOC, Identified substances, e.g. petroleum compounds, plus degradation products
	General suspected pollution	pH DO	Cat/An, DOC, DOX.

1. Field EC should be measured and recorded for all sampling. However, field EC meters are sometimes less accurate, and thus the laboratory EC is the value that is used later.
2. Temperature is usually available from the pH meter and needs to be recorded.
3. Cat/An - Full analysis of major cations and anions.
4. Microbiology - Includes the standard determinants for SANS drinking-water quality.

Where ground water contamination is known, suspected, or being investigated as part of the project, parameters specific to the waste material, history of the site/facility, disposal records, or chemicals of concern are usually (Ohio Environmental Protection Agency 2012)

3.8 Sampling frequency

The sampling frequency is determined based on different factors. Firstly, check if there are regulatory requirements/guidelines on sampling frequency for the type/nature of project you're doing. If no regulatory requirement, consult sources such as Barcelona et al (1985); U.S. EPA (1989); U.S. EPA 2009 and Timms et al (2009) to guide you on the selection of sampling frequency. The selection of the sampling frequency takes into considerations the aims of the project and hydrogeological site conditions among other factors.

For investigations of natural hydrogeochemical processes and their influence of groundwater chemistry evolution, sampling should generally cover all weather seasons to assess if there is any seasonal variations. On the other hand, determining the sampling frequency related to contamination and pollution would require a good understanding of groundwater flow rates and influence of mass/solute transportation site processes among other factors.

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CHAPTER 4 KNOW YOUR SAMPLING METHODS AND DEVICES

4.1 Introduction

In general, groundwater sampling methods can be mainly categorised into purge (active) and no-purge (passive) methods. The basis of the purging method is that stagnant water in the borehole must be removed first in order to get a sample from the aquifer formation. Passive methods collect representative samples without any purging and are based on the premise that boreholes are continuously replenished under natural flow. The main difference between the two methods is mainly in their procedures and the representativeness of the samples. A generalised classification of sampling methods is presented in Figure 3.

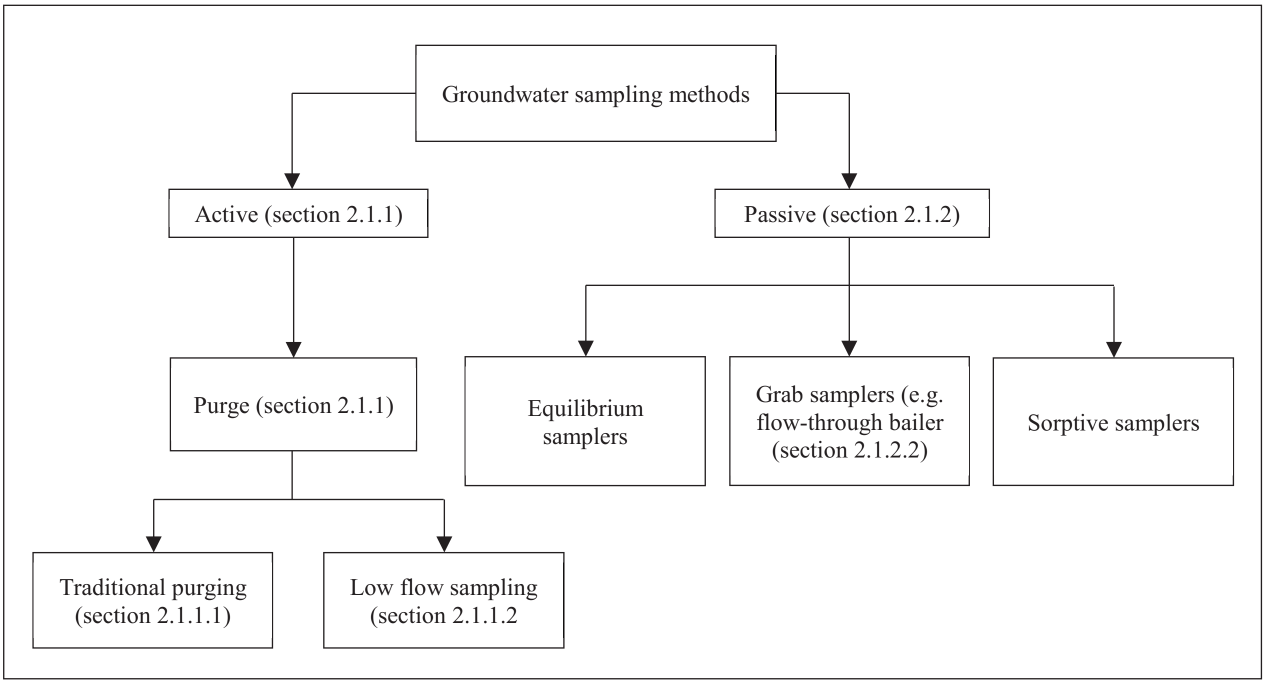

Figure 3 Generalised classification of the main sampling methods

4.2 Purge (active) method

Stagnation of water in an unused borehole modifies the chemistry of the water to the extent that stagnant water samples may be totally unrepresentative of the formation water. A borehole that has not been pumped must first be purged to remove stagnant water from the borehole so that the groundwater sample subsequently collected is representative of the groundwater drawn from the aquifer. Stagnant water can be modified by a number of processes including:

- Leaching or adsorption of certain constituents from or onto the borehole casing or screen,

- Changes of redox potential and dissolved oxygen content due to gas exchange with the atmosphere,
- Changes of microbial population as contact with the atmosphere changes anaerobic environment to aerobic. This will result in subsequent changes in pH and redox conditions and chemistry of the water,
- Precipitation or dissolution of certain metals due to changes in the concentration of certain dissolved gases such as oxygen and carbon dioxide,
- Loss of VOCs,
- Reaction of steel casing with hydrogen ions resulting in increasing pH and decreasing Eh.
- Addition of foreign materials through the top of the borehole.

In practice, the purging of the borehole involves the removal of sufficient water until the field chemistry parameters (pH, EC, DO, Eh, temperature, and turbidity) remain stable. For most cases, this involves the removal of three to five times the volume of the standing water in the borehole. The usual order of stabilisation is pH, temp, and EC, which stabilise fairly rapidly, followed by Eh, DO and turbidity (Puls and Barcelona 1996). The last three have been shown to fluctuate slightly, even after protracted purging, thus care must be taken not to be too prescriptive for parameter stabilisation criteria, especially for turbidity. We suggest that for most cases as soon as pH, temp, EC and either Eh or DO are stable, sampling can start. CL: AIRE (2008) gives an example of typical criteria to determine stabilisation of parameters during purging (Table 10).

Table 10 Example of criteria to determine stabilisation of parameters during purging

Purging parameter	**Criteria for stabilisation**
DO	± 10% of the reading or ± 0.2 mg/L
Temperature	± 0.2 ^{0}C
pH	± 0.2 pH units
Eh or ORP	± 20 mV
Electrical conductivity	± 3% of reading

Source: *CL: AIRE (2008)*

If mobile particles are thought to be contributing to the transportation of contaminants in groundwater, it is best to also include turbidity among the field parameters monitored as criteria for determining the adequacy of purging. Turbidity may be a more useful indicator of relative particle concentrations between boreholes and of stabilisation of particle concentrations during monitoring of borehole purging (Karl et al. 1994).

4.3 Traditional purge method

Traditionally, purging entails the removal of sufficient water until the field chemistry parameters such as pH, Electrical Conductivity (EC), Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), temperature, and turbidity remain stable (U.S. Geological Survey 1980) or the removal of 3 to 5 times the volume of the standing water in the borehole depending on which one comes first. Detailed guidelines on borehole purging procedures and techniques are discussed in a number of studies (Barcelona et al. 1984; Barcelona et al. 1985; Barcelona and Helfrich 1986). Specific equipment and devices used for purging are comprehensively discussed in Weaver et al (2007).

The earlier emphasis of sampling was initially on the assessment of groundwater quality of aquifers as sources of drinking water, thus traditional purging was used to sample from larger water bearing formations without concern about the potential impacts of purging rates, drawdown and dilution. However, as the general understanding of contamination and pollution in aquifers improved, a number of short comings of the traditional purging method started to emerge. Some of the main limitations of purging are as follows (Kaminski 2010):

- High purge volume can cause underestimation of maximum contaminant concentrations due to mixing induced dilution,
- High purging rates can cause overestimation due to contaminant mobilisation and increased sample turbidity,
- Dewatering of boreholes can result in losses of gaseous constituents such as, Volatile Organic Carbons (VOC), can also affect DO, methane (CH_4), Carbon dioxide (CO_2) levels, and lead to increases of sample turbidity, and
- Excessive drawdown can cause overestimation or “false positives” from soil gas or from mobilisation of soil-bound contaminants in the overlying formation or “smear zone.”

<u>Procedure for traditional purging</u>

Prior to commencing purging, examine the record sheet for the borehole. An important aspect of purging is that the purging should not drop the dynamic water-level below the main water strikes. If the water level is dropped to below this level, then cascading occurs, oxygen is introduced, gases and volatiles are lost, thus leading to erroneous results. To conduct the traditional purging method, follow the following procedure:

1. Measure the static groundwater level,
2. Measure the borehole depth,
3. Then, height of water column in the borehole = *borehole depth - depth to water level,*
4. Calculate the standing volume of water in litres by substituting in the formula:

$$V = \frac{\pi d^2 h}{4000}$$

Equation 1

Where: V = volume of standing water in litres, d = diameter of borehole in mm and h = height of water column in metres

OR Determine volume from the information given in Table 11.

5. Install the pump with the inlet close to the static water level for a high yielding borehole. (For a low yielding borehole see section 1.52 under *SAMPLING PHASE*). The pump must always be installed above the main water strike to avoid cascading,
6. Set up the EC meter, the pH meter, and the Eh or DO meter for field measurement of parameters.
7. If the site contains hazardous or potentially hazardous groundwater pollution, make arrangements to safely dispose of the purged water which may or may not contain toxic substances. Collect the purged water in the pre-arranged containers and dispose safely,
8. Start pumping,
9. Measure pumping rate in L/s,
10. Using the calculated borehole volume of step 4, calculate the pumping time needed to remove three volumes,
11. Take continuous readings of pH, temp, EC and either Eh or DO,
12. If the field chemistry parameter stabilizes before three volumes are pumped, use the time for three volumes as the purge time at that pumping rate,
13. If the field parameters have not stabilised (this is uncommon), continue pumping until they stabilize. This will be the purge time at that pumping rate,
14. Record all the above for the Monitoring Programme Guide so that succeeding sampling runs can follow this established routine.
15. Once the borehole has been purged, with the pump still running, lower the pump about 0.5 m and collect the water sample. This is done so that contamination from the stagnant water which is above the pump inlet does not occur,
16. Collect the required groundwater samples,
17. Measure the borehole depth to check that collapse has not occurred since the previous sampling run.

Table 11 Examples of borehole volumes per metre depth for different borehole diameters

Borehole diameter (mm)	Volume per metre depth (litre)
25	0.51
51	2.0
76	4.6
102	8.1
127	13
152	18
178	25
203	32
229	41
254	51
279	61
305	73

Remember that *the three-borehole volume purging approach is a traditional approach and has become less favourable mainly due to high turbidity, mixing and dilution effects, enormous amount of wastewater and energy cost, among other factors. Low-flow sampling has become more preferable in recent years.*

4.4 Low-flow sampling

In order to reduce disturbance to the borehole and formation caused by purging (bailing or high-rate/high-volume), low-flow sampling methods were developed (Kearl et al 1994, Puls and Barcelona 1996). Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the borehole screen (Puls and Barcelona 1996). The theory of principle is that one does not need to evacuate 3 borehole volumes, rather pumping at these low rates results in laminar flow *within* the borehole and mixing of fresh aquifer water with stagnant borehole water does not occur. The groundwater sample collected from the borehole screen should therefore be representative of the water from the adjacent formation.

Drawdown during low-flow purging provides the best measure of the stress imparted by a given flow-rate for a particular hydrogeological condition (Puls and Barcelona 1996). The objective is to minimise drawdown of the water column in the borehole in order to avoid disturbance of the stagnant water in the borehole screen, and draw fresh water through the screen. Stabilisation of chemistry parameters is still used to determine when formation water is accessed during purging (Puls and Barcelona 1996). During low-flow purging, flow into screen is controlled by the permeability of the formation near the borehole, regardless of pump position and high permeable zones contribute more water (Vanljen et al. 2006). In order to sample using the low-flow method, use the following procedure as a guide:

Procedure

1. Measure the groundwater static level,
2. Locate depth groundwater flow zones (fractures or water strikes) (the zones should have been screened during borehole construction),
3. Position the intake of the low-flow sampling pump opposite the borehole-screen or fracture,
4. Switch on the pump and run it at low flow rates, typically between 0.1 to 0.5 L/min. Ideally, the low-flow sampling must occur at steady state flow, that is with minimum drawdown,
5. Measure the groundwater level to check if it has stabilised, otherwise adjust the low-flow discharge rate until a steady state flow (or near steady-state flow) has been achieved,
6. Once the desired low-flow discharge rate is achieved, measure the field parameters (pH, EC, temperature, DO and ORP), continuously and collect the sample once they have stabilised,
7. Once sufficient sample has been collected, stop the pump and retrieve the equipment,
8. Clean and decontaminate (if there is need) the equipment before moving to the next sampling borehole and
9. Ensure that the pumped water is safely disposed in line with environmental wastewater regulations.

Low-flow purging *is suitable for a wide range of determinants, e.g. gases, inorganic and microbial, dissolved NAPL phases parameters*

Equipment for purging

Submersible and bladder pumps are suitable while grab samplers and syringe devices are not suitable because they cause disturbance and dislodge material from the borehole sidewall. Inertial foot-valve pumps are also suspect sampling equipment as the up and down movement will disturb fine material adhering to the sidewalls. A matrix diagram to guide the selection of suitable portable sampling devices for groundwater quality determinants is shown in Table 12.

Table 12 A matrix diagram to guide the selection of suitable portable sampling devices for groundwater quality determinants

						GROUND WATER DETERMINANDS													
						INORGANIC							ORGANIC				RADIOACTIVE		BIOL
		Device	**Approximate Maximum Sample Depth**	**Minimum Well Diameter**	**Sample Delivery Rate of Volume**	**EC**	**pH**	**Redox**	**Major Ions**	**Trace Metals**	**Nitrate Fluoride**	**Dissolved gases**	**Non Volatile**	**Volatile**	**TOC**	**TOX**	**Radium**	**Gross alpha & beta**	**Coliform bacteria**
PORTABLE SAMPLING DEVICES	GRAB	Open bailer	no limit	12 mm	variable	*			*	*	*		*				*		*
		Point-source bailer	no limit	12 mm	variable	*	*	*	*	*	*		*	*	*	*	*		*
		Syringe sampler	no limit	38 mm	0.04 - 0.75 L	*	*	*	*	*	*	*	*				*	*	*
	POSITIVE DISPLACEMENT (Submersible)	Gear-drive	65 m	50 mm	0 - 2 L/min									*					
		Bladder pump	120 m	38 mm	0 - 7.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	*
		Helical rotor	50 m	50 mm	0 - 4.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	
		Piston pump (gas-drive)	150 m	38 mm	0 - 2 L/min	*			*	*	*		*				*	*	
		Centrifugal	variable	75 mm	variable	*			*		*						*	*	
	SUCTION LIFT	Peristaltic	8 m	12 mm	0.04 - 1.1 L/min	*			*		*		*				*		*
	GAS CONTRACT	Gas-lift	variable	25 mm	variable														
		Gas-drive	50 m	25 mm		*			*		*		*				*		
IN SITU SAMPLING DEVICES		Pneumatic	no limit	not applicable	0.04 - 0.5 L	*	*	*	*	*	*		*				*	*	*

4.5 Limitations of purging

A purged groundwater sample generally reflects the average representative sample of the water drawn from the radius of influence of the borehole during purging. The patterns of the radius of influence will vary depending on the purging discharge rate, aquifer hydraulic and storage properties. Purging is particularly important for the assessments of drinking and domestic water quality because production boreholes also operate under stressed conditions. A number of setbacks with regards to purging might arise when sampling for contamination investigation purposes. Although purging can collect samples representative of water from the aquifer, it may not always reflect contaminants concentrations under the influence of natural of natural groundwater flow rates. Purging, whether it is traditional or low-flow sampling somehow induces stress in the aquifer which could result in mixing and dilution of contaminants.

A good example where such influence can occur is in fractured-rock aquifers. Fractured-rock aquifer systems can comprise one or more connected flow paths thereby increasing the potential for mixing and dilution of the purged samples (McCarthy and Shevenell 1998). In a typical Karoo single-plane fractured-rock aquifer, any form of pumping (including purging) will initially draw water from the fractures during linear flow period, then from the matrix as bi-linear flow and later radial flow (van Tonder et al., 2002). These different flow regimes can lead to the mixing of groundwater prior to sample collection (Gomo and Vermeulen 2015).

Don't purge when *it is necessary to observe whether or not floating and/or sinking organic compounds such as diesoline, gasoline, petrol etc. are present. For this purpose, use a bailer made of clear material so that the thickness of the floating organic compounds (LNAPLs) can be measured. For sinking chlorinated solvents (DNAPLs) such as carbon tetrachloride (CCl_4), a clear bailer is used to collect a sample at the bottom of the monitoring borehole.*

4.6 Passive (No-purge) methods

Passive/non-purge sampling has also been gaining popularity as a low-cost alternative to purging (Vroblesky and Hyde 1997; Parsons 2005; U.S. Environmental Protection Agency 2010; Interstate Technology & Regulatory Council 2008; Savoie and LeBlanc 2012). Under natural conditions, groundwater from the adjacent aquifer formation continuously flows across the borehole through the screened casing (Robin and Gillham 1987) and this present an opportunity to collect representative groundwater samples without purging. A passive sampler can therefore be used to obtain representative groundwater sample from discrete depths (flow zone) in a borehole that is naturally replenished without actively inducing stress into the aquifer media by pumping or purge techniques. To facilitate continuous replenishment of water in the flow zone interval, the monitoring borehole has to be open or screened along groundwater flow zones. Location of the discrete groundwater flow zones prior to the collection of groundwater samples is therefore very important. The common no-purge methods include diffusion sampling and grab samplers (Savoie and LeBlanc 2012).

Based on the mechanism and nature of the collected sample, Interstate Technology & Regulatory Council (2007), classifies groundwater passive samplers into three general types:

1. **Equilibrium samplers** – There are deployed into the borehole at the depth of interest and analytes diffuses across the sampler membrane to establish and maintain equilibrium with the sampled medium,
2. **Sorptive samplers –** Deployed into the borehole at the depth of interest and through diffusion and sorption, analytes to accumulate in the sampler over time,
3. **Grab samplers** - Devices that collect water samples at a specific depth and time. **In South Africa**, the *flow-through stainless steel metal bailers are a common example* of grab passive samplers.

Considerations for passive/no-purge sampling

Interstate Technology & Regulatory Council (2007) and ASTM (Standard D7929-14 - ASTM, 2014) discusses in comprehensive details important factors to consider when selecting passive samplers option, only a summary for quick guide is presented in Table 13.

Table 13 Important factors to consider when selecting passive sampler option

Factor	Applicability/considerations
Applicable analytes	Suited for VOCs but slowly being adapted for inorganic chemistry (see the given references for specific analytes)
Data Quality Objectives (DQOs)	Identify and agree with the team on site-specific DQOs, data evaluation techniques prior to implementation
Depth of deployment	At flow zones where there is exchange between the borehole and aquifer (determined through vertical chemical profile)
Borehole construction	Screened or open borehole sections
Sample volume	Limited volume, collect enough and extra for quality control or assurance purposes
Groundwater flow characteristics	High groundwater flow rates to enable replenishment of borehole (See the references given for assessing the sufficiency of flow prior to deployment)
Vertical flow in the borehole	Use discrete interval sampling

Contaminant Stratification	Use multiple samplers in series, at discrete intervals within the screened water columns or open interval (Depths of deployment determined through vertical chemical profile).

Important benefits and challenges of passive samplers are summarised in Table 14 (Interstate Technology & Regulatory Council 2007, ASTM, 2014 and Stroo et al 2014).

Table 14 Benefits and challenges of passive samplers

Benefits	Challenges
Can be used where access is difficult or where discretion is desirable	Some passive samplers are not used on all the be used for all analytes
Can be deployed in series to provide a vertical contaminant profile	Some samplers are not appropriate for “total” unfiltered sample analysis due to diffusive filtration
Not limited by depth	Maximum collected volume is limited
Reduction of data artefacts associated with purging (e.g., excessive drawdown, mixing, turbidity ….)	Requires identification of sufficient ambient flow in the borehole screen zone prior to deployment
Cost savings from reduced sampling time and decreased waste generation	Some methods (i.e., Sorptive methods) gives calculated concentration rather than the measured one

It has been shown that in some cases, passive samplers can obtain samples that are very comparable to purging and or low-flow sampling for a number of determinants (e.g. Byrnes et al. 1996, Lundegard et al. 1997, Springer 1998, Interstate Technology & Regulatory Council (2007), Stroo et al (2014), ASTM (Standard D7929-14 -ASTM, 2014). Borehole specific evaluations are, however, recommended before the adoption of the bailer.

Do not *use passive samplers if the aim is to analyse for microbial chemistry related determinants.*

Grab samplers

Grab samplers can collect groundwater samples at discrete depth without pumping or purging.

Bailers

Bailers are generally popular because of their portability and simplistic of use. They are made of inert materials such as Teflon, stainless steel, polyvinyl chloride (PVC), polyethylene, and polypropylene. Plastic bailers are often disposable thus eliminating the need to decontaminate. This also minimises the risk of cross-contamination.

Although expensive, stainless steel bailers are reusable and therefore locally more popular. Stainless steel can resist corrosion, heat damage and chemical damage thus reduces the chances of contaminating the groundwater. The bailers are cylindrical in shape (shape of a borehole), the length varies but typically not more than 1 m. The diameter of the bailers should be able to fit into a piezometer/borehole or borehole. There is probably no standard dimension for bailers. The Ohio Environmental Protection Agency (2012) recommends a bailer diameter of ≤ 75% of the inside diameter of the borehole casing to allow for adequate clearance. A code is used to lower and raise the bailer but also to open and close the valves. This code must also be inert to the reaction effect of contaminants/pollutants. A summary of basic information on the bailer grab samplers is given in Table 15.

Table 15 Summary of basic information on the bailers samplers

Bailers		
Type of bailer		Determinant suitability**
Top-filling	Valve at top is open at the desired sampling depth. Water enters the bailer through the top	Non-aqueous phase liquids (LNAPL)***
Single check (Bottom-filling)	Check valve at the bottom allows allow water to flow into the bailer. Valve closed by the weight of the water on retrieving the bailer.	Dense, non-aqueous phase liquids (DNAPLs)*** and in some cases inorganic chemistry parameters
Flow-through (Double check)	Bailer lowered into the water with both top and bottom valves open. Water flows through the bailer minimizing disturbances. At desired depth, both valves are simultaneously closed and bailer is retrieved.	Dense, non-aqueous phase liquids (DNAPLs)*** and in some cases inorganic chemistry parameters

*The operating skills and consistency of the sampling personnel is very important. Inconsistency could lead to variability of the sampling results;

**For inorganic chemistry parameters, borehole specific evaluations are important to determine the appropriate sampling techniques and or tools

*** Use transparent bailer in order to measure the thickness of the product

Locally, stainless flow-through and top-fill bailers are some of the commonly used, thus a description on their operation procedure is given below.

<u>Flow-through bailer</u>

The bailer has a valve at the top that is pulled to open both the top and the bottom part of the bailer such that the water can flow through during lowering of the bailer thereby minimum mixing or disturbances of in-situ conditions. The opening valve is controlled manually with the use of a cord (rope) that is tied to the inbuilt hock on the valve. The following steps can be used to collect a groundwater sample with this type of bailer:

1. Measure lengths of the two codes equivalent to the desired sampling depth and put markers.
2. Tie one cord on a hock placed on the bailer.
3. Tie the other cord on opening valve via a hock placed at the top of the valve,
4. Put on your grip gloves for handling the cord.
5. Pull the valve controlling cord to open the top and bottom of the bailer before deployment into the borehole.
6. Deploy the bailer into the borehole by lowering the two ropes, to ensure that the bailer remains open throughout the deployment maintain tension in the valve controlling rope while the rope on the bailor itself is loosened.
7. Once at the desired depth, the top and bottom openings of the bailer are simultaneously closed by loosening the valve controlling cord and tensioning the cord tied on the bailer.
8. Lift the bailor to the surface by pulling the tensioned cord tied to the bailor in order to retrieve the sample.
9. Retrieve the two cords but ensure that the bailer remain closed throughout the lifting by keeping the bailer tied cord tensioned and the valve controlling cord loosened.
10. Once at the surface, open the valve to drain the groundwater via the bottom of the bailer into the prepared and labelled sampling bottles. Fill to the bottles to the top to eliminate air.
11. Drain the other water into beakers for measurement of field parameters. The sample is most likely going to interact with the air during draining from the bailer, thus those field parameters sensitive to degassing are going to be affected. It is still very important to measure all field parameters possible; they might provide other insights on the hydrogeochemical conditions of the aquifer.
12. After sufficient water is sampled, rinse the bailer and wash the ropes with deionised water.
13. If the sampled groundwater is contaminated, decontaminate the bailer using guideline.
14. Depending on the level of contamination, the sampling cords might be difficult to decontaminate, safely disposing them is much more convenient but could be costly to replace on each sampling borehole.

Top-fill bailer

The bailer has an opening at the top that is opened and closed with a valve. The valve is controlled manually by the sampler with the use a cord tied to a hock on the valve. To collect a groundwater sample with this bailer follow these steps:

Step 1-4, follow the procedure given for the flow-through bailers,

5. Prior to deployment, ensure that the bailer is closed,
6. Deploy the bailer into borehole using the cord tied to the bailer, to ensure that the bailer remains closed throughout the deployment, maintain tension in the cord tied to the bailer while the valve controlling cord is loosened,
7. Once at the desired depth, open the valve by pulling up the valve opening cord and loosening the bailer tied rope,
8. Allow reasonable time (can be easily established with experience and is also a function of bailer size) for the bailer to be completely filled,
9. Once the bailer is fully filled, close the valve by loosening the valve controlling cord and tensioning the cord tied to the bailer to lift the bailer back to the surface
10. Lift the bailor to the surface by pulling the tensioned cord tied to the bailer, ensure that the bailer remain closed throughout lifting by keeping the valve controlling rope loosened,
11. Steps 11-13, follow the procedure given for the flow-through bailers.

Remember that *for each type of the passive samplers, there are a variety of products which also keeps changing due to technological advancement. It is there difficult to try and give a detailed description for each of these products in terms of their deployment, capabilities, benefits, limitations and challenges in this manual. For more details on these issues, readers are must consult studies such as Interstate Technology & Regulatory Council (2007), Stroo et al (2014), ASTM (Standard D7929-14 - ASTM, 2014) among others that addresses the subject in comprehensive details. At the same time, these sampling devices are accompanied by the manufacturer's instructions or operation manual that you must always use.*

Recommendations on the use of passive samplers

It will be difficult to prescribe in this manual which hydrogeological conditions exactly suit the application of passive samplers. The ability of the passive samplers to collect representative samples depends on a number of conditions and requirements (Table 13) (Interstate Technology & Regulatory Council 2007, ASTM, 2014 and Stroo et al 2014). The adoption of passive samplers cannot therefore be recommended without some minimum considerations. The following steps are suggested as a guide (Gomo et al. 2017):

- Conduct site-specific evaluations for each borehole before passive samplers can be adopted,
- Evaluations can be based on the analysis of variance (ANOVA) between all-important determinants (according to the monitoring programme and project goals, but not for microbial

parameters) measured in bailered and purged samples at a 99% confidence interval. At this confidence interval, adoption of bailers can be scientifically justified if;

  - ✓ There is statically no significant difference between the two groups and
  - ✓ There is at least a 99% probability that the observed statistical difference (even when they are not significant – indicated by the p-value) is attributable to random chance and not to the influence of sampling methods (tested factor).

- When passive sampling has been adopted for long-term monitoring, comparison must be made to the low-flow purging sampling during their use. The interval for comparison would probably vary due to factors such as site conditions and monitoring frequency, among others. Comparisons at the start, middle and end of the monitoring programme would help to assess the performance of the passive methods to purging, and
- For once-off sampling exercises and sampling for analysis of microbial analytes low-flow purging is highly recommended.

4.7 Sampling equipment and devices

A matrix diagram to guide the selection of suitable portable sampling devices for groundwater quality assessment determinants is presented in Table 12. For detailed information, the following sources can be consulted: Pohlman and Hess 1988; Interstate Technology & Regulatory Council 2007; Weaver et al. 2007; Interstate Technology & Regulatory Council 2008; Sundaram et al. 2009; Ohio Environmental Protection Agency 2012 and Stroo et al 2014 among others.

Sampling equipment and devices *must be constructed of inert components which are resistant to contaminants or pollutants reaction effects*

4.8 Direct push technology (DPT)

This section only gives a brief description of DPT sampler principles and application. Comprehensive details can be found in the primary sources of information for this section (U.S. EPA Office of Solid Waste and Emergency Response (2005) and ASTM D6001 - 05(2012).

The working principle of DPT sampler is that a groundwater sampling or monitoring point/station (borehole/borehole/piezometer) can be quickly installed in unconsolidated formation without the expense of having to first drill and construct an open borehole. Bailers or pumps can be used to collect groundwater sample from the DPT sampler, or the sampler itself can be retracted to the surface to obtain the water sample. Components of the DPT sampler must be made up on inert materials to prevent reactions with sampled constituents. Sampling equipment for DPT is mainly grouped into two main categories of Point-in-time groundwater samplers and DPT-installed groundwater monitoring boreholes.

> **Point-in-time groundwater samplers** – designed to rapidly collect groundwater samples to define groundwater hydrogeochemistry or quality conditions during one sampling event, ideal for preliminary site characterisation.
>
> **DPT-installed groundwater monitoring boreholes** – Samples are collected from monitoring boreholes that have been installed using the DPT for short, medium or long-term monitoring.

Table 16 gives a general guideline on the factors to consider when deciding on the suitability of using DPT. The factors are not arranged according to priority or the most important. It will be up to groundwater practitioner to rank the factors in line with sampling goals of the project.

Table 16 General guideline on where and where not to use DPT

When is DPT preferable?	When to avoid DPT?
Preliminary site characterisation to improve site decision making and planning for detailed work	Aim is to assess for drinking and domestic drinking water quality
Access to drilling sites is limited	Hard rock and too soft formation
Depth discrete samples are required	Average weighted samples are required
Vertical profiling for generating three-dimensional profiles	Deep investigations (check equipment specifications
Minimise waste generation, thereby reducing exposure risk to harmful/toxic substances	High concentrations of contaminants near or on the land surface
Unconsolidated aquifer and unsaturated zone material – but not too soft like shale	Large volumes of soil and groundwater required for analytical purposes
Small soil and groundwater volumes are sufficient for the analytical purpose	Monitoring boreholes are further required for test such as pumping or tracer tests
Wider presence of cohesive soil at the site	
Site is contaminated	
Soil samples are desired from the aquifer	
Delineation of contamination plume is required	

4.9 Sample containers

The size of the sampling containers is mainly a function of the analytical method to be used. Always consult the analytical laboratory about the appropriate sampling containers, sample volumes and any specific preservation for their analytical methods. A guide on appropriate sample containers suitable for different determinants is presented in section 0 of the sampling phase.

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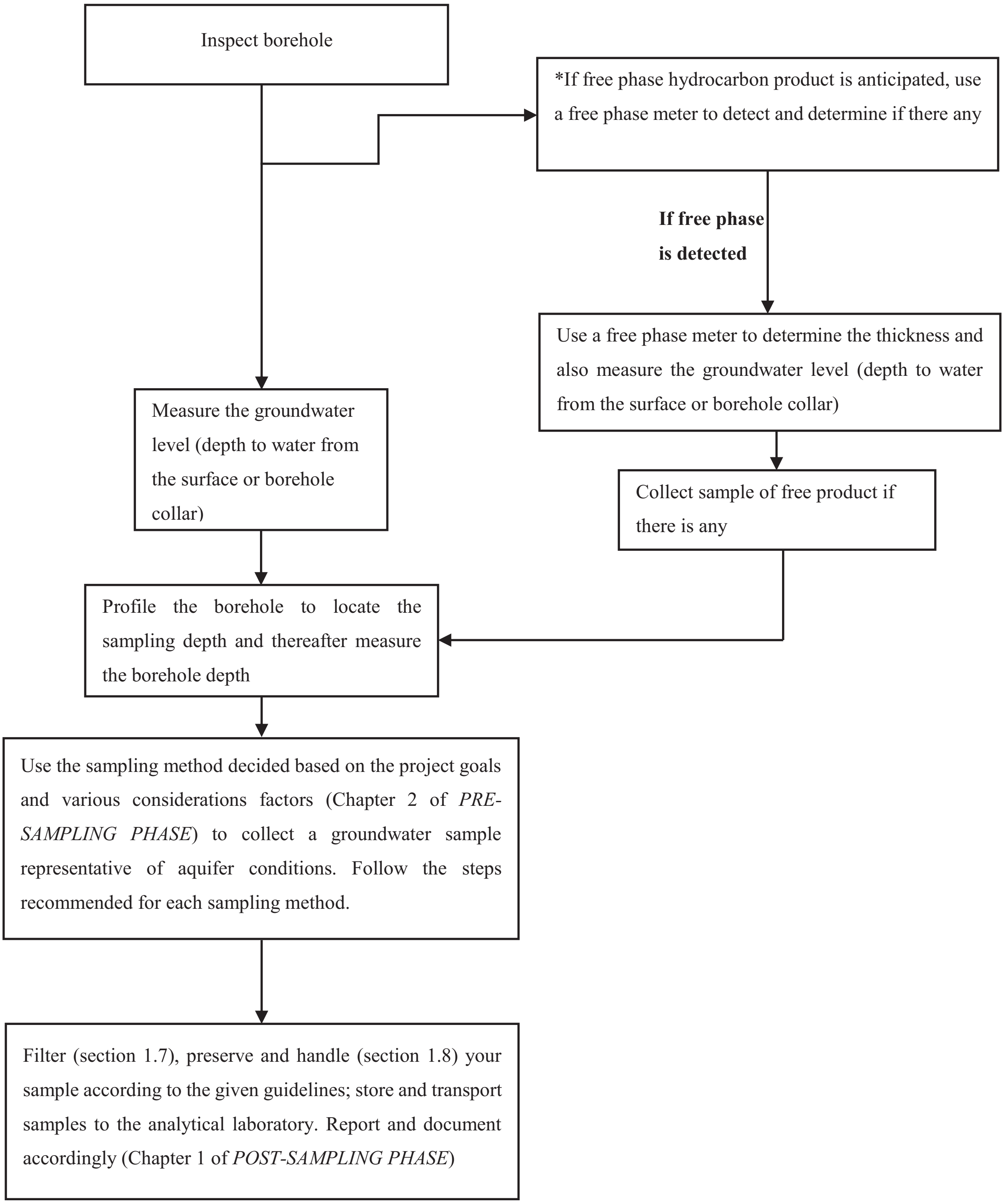
A decision tree diagram showing the general field procedure to guide the collection of groundwater samples is presented in Figure 4.



*If free phase hydrocarbon product is anticipated, use a free phase meter to detect and determine if there any

Use a free phase meter to determine the thickness and also measure the groundwater level (depth to water from the surface or borehole collar)

Collect sample of free product if there is any

Measure the groundwater level (depth to water from the surface or borehole collar)

Profile the borehole to locate the sampling depth and thereafter measure the borehole depth

Use the sampling method decided based on the project goals and various considerations factors (Chapter 2 of *PRE-SAMPLING PHASE*) to collect a groundwater sample representative of aquifer conditions. Follow the steps recommended for each sampling method.

Filter (section 1.7), preserve and handle (section 1.8) your sample according to the given guidelines; store and transport samples to the analytical laboratory. Report and document accordingly (Chapter 1 of *POST-SAMPLING PHASE*)

(* Free phase hydrocarbon is that component of the hydrocarbon product that floats on top of water)

Figure 4 General Field procedure to guide the collection of groundwater samples

CHAPTER 5 GENERAL FIELD PROCEDURE

5.1 Borehole inspections

It is important to inspect the borehole before opening and after opening to ensure that it free of obstacles and therefore safe to use.

5.2 Detection and sampling of free phase hydrocarbon products

If there is any free phase hydrocarbon component floating on top of the water, an interface meter can be used to detect it. There are different types of interface meters on the market, but they generally operate using the same principle of operation. The probe of the meter would make different sounds depending if it is in contact with the product or water and from this the thickness of the free phase can be determined. The free phase component can be sampled using a clear top fill bailer.

5.3 Groundwater level measurement

Groundwater level is measured within a borehole as depth to the water below the ground surface or borehole casing. The unit for groundwater level is often meters below ground level (mbgl). It is a basic property which must be measured before any purging or sampling, but also for each sampling event. The groundwater level measured is the static water level assumed to be without the influence of pumping. Groundwater levels are important for determining hydraulic head distributions, hydraulic gradient, groundwater flow and contamination migration direction and rates in the aquifers. Long-term monitoring of groundwater levels is important for understanding the temporal responses of the aquifer to rainfall and determination recharge among other aspects. Groundwater recharge can influence hydrogeochemical processes of aquifers in a variety of ways (Adams et al. 2004; David and Pyne 2005).

Remember that *the hydraulic head which is determined based on the measured groundwater water level is a general reflection of pressure within the aquifer, thus the information about the borehole construction is crucial to show which aquifer is being measured.*

There is a wider range of devices that can be used to measure the groundwater level (Garber and Koopman 1978). Electronic water level indicators are by far the most common ones. For long-term or continuous measurement of groundwater levels pressure transducers and a wider of automatic digital data loggers have become much more popular.

5.3.1 Electronic water level meter

There is a wide range of electronic water level meters in the market. The instrument typically consists of a probe attached to the end of double conductor wire; and an indicator light. When the probe comes in contact with the water, the circuit is closed and an indicator light is illuminated accompanied by a whistle. Groundwater water level readings are taken directly from the tape at the top of the borehole casing. Electronic water level meters come in different forms/designs; some combine Temperature Level and Conductivity (TLC) (See example in Figure 5) while others measure only the level (Dip meter).

Source: www.solinist.com

Figure 5 Example of a TLC meter

Procedure:

1. Switch on the electronic water level meter and lower the probe or sensor into the borehole/piezometer by unwinding the tape from the holder,
2. When the probe touches the water, the electronic water level meter will give a signal such as sound, light illumination and others depending on the design. Always refer to the manufacturer's operation manual for appropriate use of the equipment,
3. When the meter gives the signal that the probe has touched the water, read the depth to water from the borehole casing (groundwater level) on the meter's tape. Pull up the probe and repeat the measurement to verify,
4. When the measurement has been verified through the second reading, retrieve the tape of the meter by winding it back on the holder. Ensure that the tape of the meter is not damaged by the borehole casing during lowering and retrieval because that can also damage the conductors that enable the meter to function, and

5. Clean and/or decontaminate the groundwater level meet accordingly before its use at the next sampling borehole.

5.3.2 Home-made manual water level meter

There is a variety of home-made manual water level meters, but only two of the simplest devices will be mentioned here.

Plopper

A plopper is a smallish cup-shaped weight, attached to the measuring tape via a hock placed on top of the plopper (Figure 6, Sundaram et al. 2009). The plopper is closed at the top and opens at the bottom. Stainless steel is often used to make the plopper, but any other inert material can be used.

Source: Sundaram et al. 2009

Figure 6 A Plopper for measuring groundwater level

In order to measure the groundwater levels with plopper, use the following procedure:

1. The plopper is lowered into the borehole by unwinding the tape off the holder and when the down-pointing cup touches the water or NAPL layer a “plop” sound is heard.
2. On hearing the plop, a reading is taken from tape attached flow. This is repeated a few times to be sure the correct liquid level is being measured.
3. After verifying with at least two repeatable readings, the plopper is retrieved back to the surface, cleaned and or decontaminated before going to the next sampling borehole.

Whistle level meter

It consists of open ended tube with a small hole at the top which hangs from a tape measure. When it comes in contact with water the air is pushed through the hole and a sharp whistle sound is made. When the sound is made, the depth to water measurement is read on the tape measure.

5.3.3 Water level in borehole equipped with a pump

When the borehole to be sampled is fitted with a production pump, access to the water level must be open. The pump riser main, the electrical cabling and the safety rope for the pump usually create a tangled mess, and if you try to lower the dip-meter cable inevitably it will get stuck. If this is a borehole that will be sampled on a regular basis then a piezo-tube must be fitted in the borehole.

This is a small diameter pipe installed from borehole-head to some distance below the expected lowest water level in the borehole. This is securely attached to the riser main of the pump. The diameter of the pipe can be 20 mm to 25 mm, or similar size. The pipe diameter must be able to take the dip-meter cable and the attached weight. This pipe allows the water level to be accessed without danger of getting stuck in the open borehole. The material of the pipe must be inert.

In production boreholes, *continuous monitoring with pressure transducers and automatic digital is advised. However, manual measurement is still vital for verification and in the case of technology failure.*

Always use *the same reference point (datum) for measuring the groundwater level at each borehole throughout the monitoring period for comparison purposes.*

5.4 Determination of the sampling depth

Appropriate location the sampling depth is a very critical stage for groundwater sampling of dissolved analytes. There is a variety of designs for monitoring boreholes/piezometer to suit different sampling needs and site conditions (Johnson 1983; Black et al. 1986; Jones and Lerner 1995; Lerner and Teutsch 1995). The manual is not intended to cover the design of monitoring network and boreholes in any detail. In some of the monitoring borehole designs, the sampling level or depth will be known before sampling from construction and design reports.

There is, however, a number of monitoring boreholes which are either open or screened throughout the entire depth “long screens”. In such cases, profiling (logging) the borehole can help to locate discrete groundwater flow zones which can then be targeted for sampling. Profiling tools uses different parameter principles of operation. Such parameters principles include; Reduction potential (Eh)/Oxidation Reduction Potential (ORP), Dissolved Oxygen (DO), pH, Fluid Electrical Conductivity (FEC) and temperatures among others. The FEC profiling parameter which is has overall dependence on the presence of ions, their total concentration, mobility, valence, and relative concentration is more commonly used. Manual Temperature Level Conductivity (TLC) meter is often used for both groundwater level measurements and FEC profiling. Automated TLC data loggers are now available

5.4.1 FEC borehole profiling or logging

For profiling, the parameter of interest is measured with depth. Depth interval of at most 10 cm is recommended for more refined results. In the example of FEC profiling, the change (also referred as anomaly) in the magnitude of the FEC with depth is inferred to indicate a zone (position) of contrasting groundwater chemistry. With the help of the borehole lithological logs, borehole construction and site hydrogeological conditions, discrete positions of contrasting FEC along the depth profile reflecting groundwater flow zones can be identified and are targeted for sampling.

Discrete groundwater flow zones are generally associated with fractured-rock aquifers. In such aquifers, fractures are highly permeable relative to the matrix. Along fractures, natural groundwater replenishment is frequently expected in the borehole in comparison to low permeable matrix zones. Due to this difference in replenishment characteristics, some contrasts in groundwater inorganic chemistry as reflected by the FEC are expected between high and low permeable zones. Groundwater flow zones are therefore targeted for sampling because the water in the screened or open part of the borehole is continuously inferred to be replenished hence is expected to reflect the hydrogeochemical conditions of the water in the aquifer and not stagnant water in the borehole. Fractured-rock aquifers widely occur in South Africa. However discrete groundwater flow zones can also occur in other aquifers such as layered alluvial aquifers, weathered basement aquifers among others.

The nature of FEC contrasts along a depth profile mainly depends on the hydrogeochemistry characteristics of the groundwater transmitted in the flow zone, structure of the aquifer and groundwater flow properties. As part of this project to update the GSM, laboratory studies were undertaken to investigate typical FEC depth profiles in a typical horizontal single-plane fractured-rock aquifer as function of the groundwater quality being transmitted. Tap water and saline (table-salt added) water were used to simulate fresh and contaminated water flow conditions respectively.

5.5 Examples of FEC profiles associated with a plume in a typical horizontal single-plane fractured rock aquifer

FEC profiles associated with a plume in a typical horizontal single-plane fractured rock aquifer are presented in this manual to illustrate the changes that can occur in one aquifer system due to the influence of changing hydrogeochemical conditions. A horizontal single-plane fractured rock aquifer consists of single horizontal fracture as the main transmissive and transport layer and in surrounded by matrix of typically high storage and low transmissivity. Figure 7 shows laboratory measured FEC profiles associated with a plume in a typical horizontal single-plane fractured rock aquifer. The fracture position is from 5-8 cm depth. The purpose of Figure 7 is to illustrate the changes in the shape of the FEC profile as influenced by different hydrogeochemical flow conditions and not to show the actual changes of the FEC values.

From the FEC profiles associated with a plume in a typical horizontal single-plane fractured rock aquifer, it is clear that the shape of the profile is largely dependent on the hydrogeochemical quality of the water being transported by the groundwater flow zone. The hydrogeochemical conditions could be influenced by a number of factors. For example, a plume of dissolved contaminants could raise the FEC at the flow zone as the plume passes the borehole thereby changing the shape of the FEC profile and this happens can occur again during the plume the dilution process. Recharge, for instance might replenish the aquifer with fresh water, thereby lowering the FEC at the flow zone and the profile shape could change again. It is clear FEC profile shape in a single borehole can change depending on hydrogeochemical conditions. Borehole FEC profiles should therefore be used with caution and based on understanding when locating groundwater flow zones which are then targeted for sampling. One should also remember that other profiling parameters (e.g. temperature, ORP, DO and pH among others), will also have their own different characteristics anomaly associated with the groundwater flow zones as a function of the aquifer structure and hydrogeochemical conditions of the groundwater.

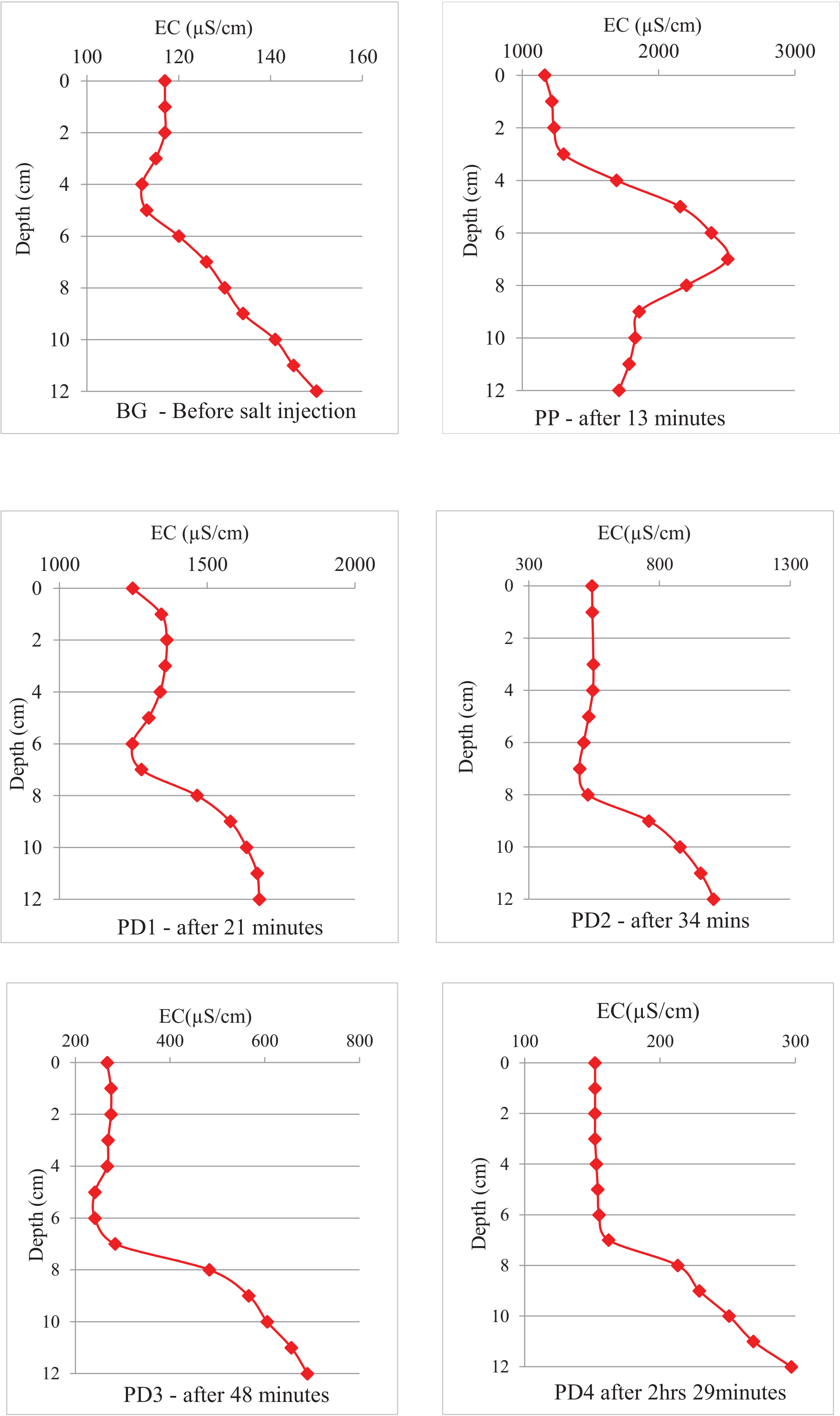


Figure 7 Laboratory measured FEC profiles associated with a plume in a typical horizontal single-plane fractured-rock aquifer; BG – background profile before injection of plume, PP – Plume peak profile,

PD1 – First profile after plume dilution, ..., PD4 – Fourth profile after plume; fracture position is from 5-8 cm depth.

Points to remember for locating the sampling depth of interest

- *It is difficult to investigate FEC profiles in all aquifer types and associated with different contaminants, and this given information should only save as an illustration of the changes which might occur.*
- *Groundwater flow and hydrogeochemical characteristics are highly heterogeneous, thus the FEC (or other parameters) profiles will vary from one site to the other and also from time to time.*
- *It is therefore important for the groundwater practitioner conducting the sampling or data interpretation to investigate and understand the FEC profile characteristics associated with the borehole in order them to appropriately determine the sampling depth.*
- *The groundwater practitioner must therefore interpret the meaning of the profile anomalies with respect to their site and decide where to collect their representative sample at a particular time.*
- *The sample must reflect the in-situ chemical and microbial status of the groundwater at the time of sampling and location of sampling within the aquifer.*

5.6 Collection of representative groundwater water samples

Reasons for groundwater sampling vary from one project to another and from site to site. One thing that does not change *is that the collected sample must be representative of the water coming from the aquifer*. This is very important because the objective is to chemically characterise the water in the aquifer and not the stagnant water in the boreholes. There are two main methods used for collecting representative groundwater samples, active (purging) and passive methods (Chapter 2 in *PRESAMPLING PHASE*).

Depending on factors such as site conditions, project and monitoring goals, research has shown that in some cases both methods can be used to collect equally representative samples. It must, however, be emphasised that there is no "one size fits all" when it comes to the sampling methods. Selection of an appropriate sampling method will, therefore, have to consider a variety of factors. Some of the most important factors to guide in the selection of an appropriate sampling method are presented in Table 17.

Table 17 Factors to consider when selecting a suitable sampling method

Sampling method	When is the method more suitable?
Traditional purging	1. Assessment of groundwater quality for drinking and domestic uses 2. Analysis for microbial analytes 3. Deep and shallow aquifers 4. Investigation of natural hydrogeochemical 5. High permeable aquifers
Low-flow sampling	1. Contaminated aquifers (minimise mixing and dilution of contaminants while reducing generated waste-water) 2. Deep and shallow aquifers 3. Low and high permeable aquifers 4. Analysis for microbial analytes
Passive	1. Contaminated and polluted sites 2. Discrete groundwater samples 3. High or low yielding aquifers 4. Deep and shallow aquifers

5.7 Sampling from low yielding boreholes - Purge dry and collect sample

Some boreholes drilled into low yielding aquifers and can run dry during purging even at low-flow discharge rates. Allow the borehole to recover until it has accumulated sufficient water to enable sample collection. The sample can be analysed for many parameters but certainly not those susceptible to the effects of degassing or air exchanges with the atmosphere. The samples can also be limited by a number of challenges which includes (Nielsen and Nielsen 2002; U.S. EPA 2001):

- During a prolonged recovery, exchange of dissolved gases with the atmosphere would affect the redox state of the groundwater thereby affecting the concentration of some analytes such as dissolved metals,
- In addition, the cascading effects of recovery water can result in the loss volatile organic constituents if any are present; the approach is therefore not suitable for sampling of gases and,
- Sample chemistry in a borehole might be affected during borehole recovery through prolonged exposure to atmospheric conditions.

5.8 Sampling deep boreholes

Boreholes of depth greater than 100 metres below ground level (mbgl) are generally regarded as deep. Sampling from such boreholes could require different set of equipment and approach than the ones typically used for shallow boreholes. The objective is always to collect a sample representative of aquifer water and not stagnant water in the borehole. Pumps are now available to which extension tubing can be installed to the pump intake in order to reach the desired sampling depths. Some of the pumps are also designed to operate out of the water.

Deep borehole sampling aspects *are addressed in more detail by Sundaram et al. 2009.*

5.9 Sampling from production boreholes

When collecting groundwater samples from production boreholes, the decision tree in Figure 8 will be useful. It is important to purge when collecting groundwater samples for drinking and domestic water quality assessments in order to obtained an average weighted sample.

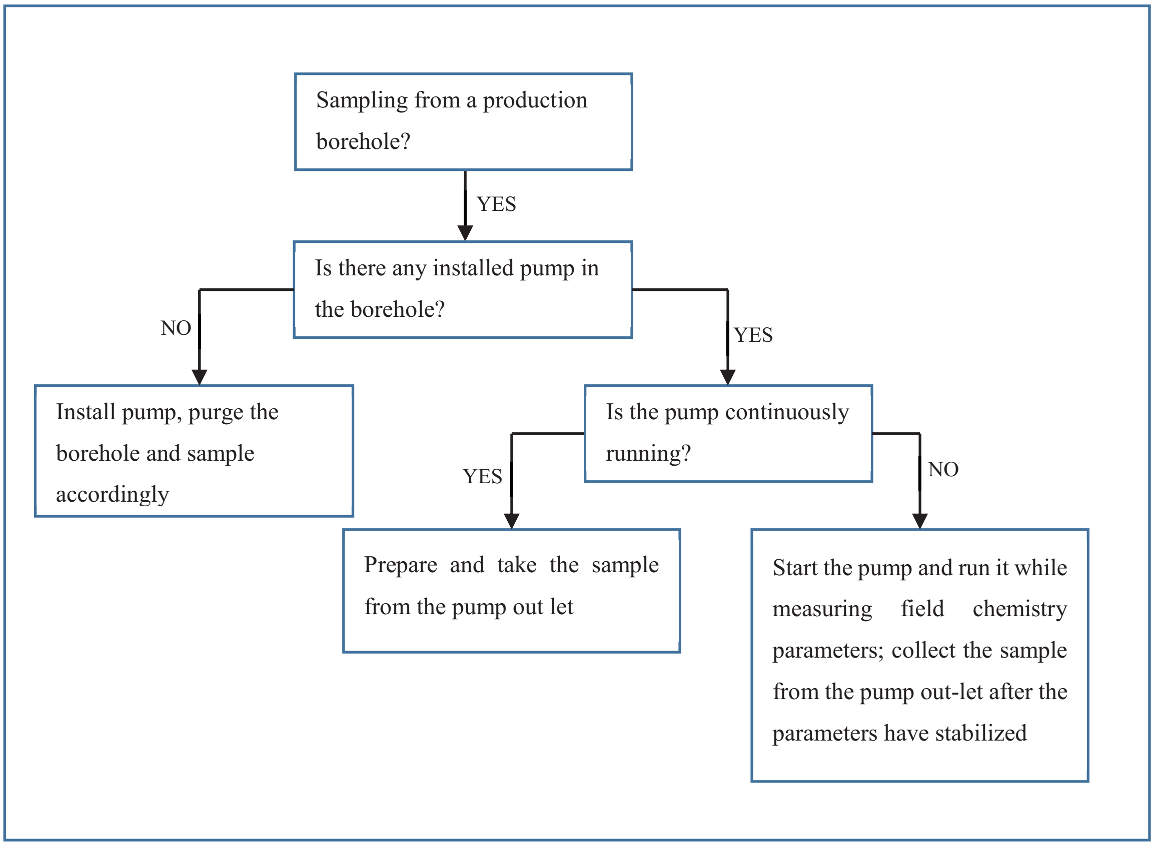


Figure 8 Decision tree to guide when sampling from production boreholes

5.10 Measurement of field parameters

Field parameters are those which parameters which must be measured in the field before or during the collection of the samples. The aim is to achieve a measurement which reflects hydrochemistry characteristics of aquifer water before it is subjected to external influences while on the way to the laboratory for analysis. The most important field measured parameters are pH, temperature, redox potential (Eh), electrical conductivity (EC), dissolved oxygen (DO), alkalinity and acidity. The selection of field parameters measured will depend on the goals of the monitoring.

There are many types of meters/probes on the market to measure field parameters, many with different features and operating procedures to those described in this manual. It is very important to read the manufacturer's instructions on the correct calibration, operation and maintenance procedures for the particular instrument. Some of the equipment and procedures described here may not be applicable for the instrument. If so, make sure you understand the manufacturer's instructions and adapt the given guidelines accordingly.

It is important to highlight that for temperature measurements, most meters for the other parameters are compensated for temperature, thus they should also give you a temperature reading. You would therefore not need a separate meter/probe for temperature. It is, however, important to check the type of measurements each equipment can give.

The general procedure for any of the equipment measurements described in this section is its calibration and then use to take field measurements. Always follow the manufacturer's instructions for calibration, use procedure, care and maintenance of the equipment. The general guide with regards to the measurement of field parameters that you must know is given in Figure 9.

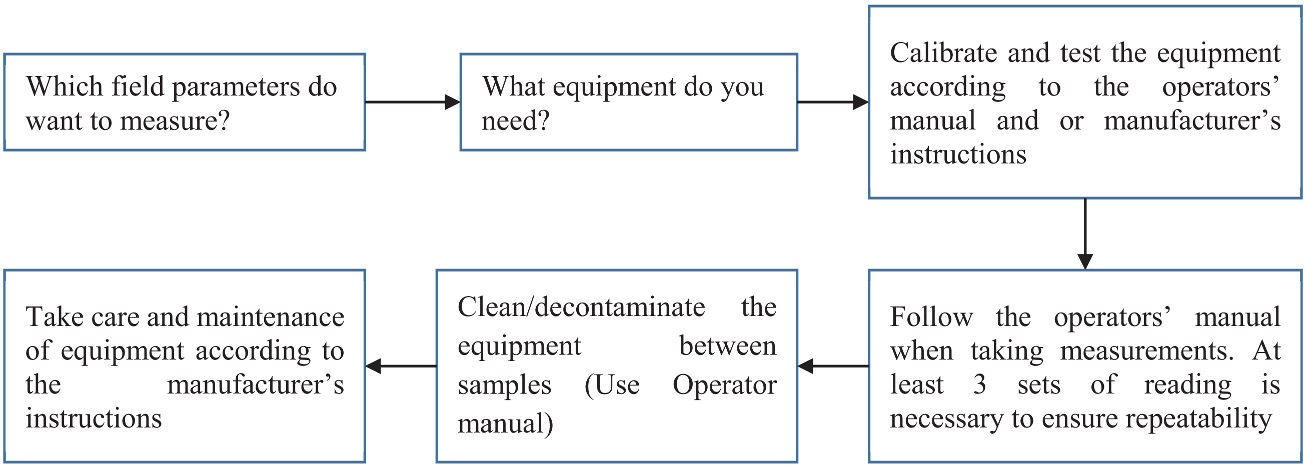


Figure 9 General guide to the measurement of field parameters

5.10.1 pH

pH is a measure of the concentration of hydrogen ions in solution. These concentrations in natural waters are generally very low and vary over many orders of magnitude, which make it more convenient to report them on a logarithm scale, rather than as absolute concentrations. By definition:

$$pH = -log_{10}[H^+]$$

Equation 2

Typical modern pH meter/probe is a combination electrode, which is made up of both the glass and reference electrodes into one-unit equipment. There is a variety of pH meters probes in the market. While the technological aspects of the equipment continue to improve their basic principle of operation is basically similar. The most important component is electrode, which therefore need proper care and maintenance. Use the manufactures instructions on the use, care and maintenance of the electrodes.

<u>Equipment</u>

pH can be determined by electrometric or colorimetric methods. Electrometric methods use either a glass electrode or an ion sensitive field effect transistor (ISFET). Colorimetric methods use pH indicators (e.g. litmus paper), which change colour with a change in pH. Colorimetric methods are only suitable for very rough pH estimates (±2 units) and are generally not recommended for groundwater investigations.

For groundwater general field use, a pH meter is recommended. This is a combination electrode which incorporates the measuring and the reference electrodes into a single probe available in a robust plastic envelope. Besides the pH meter itself, one needs the following:

- Sample bottle,
- Flow through cell,
- Extra batteries for the meter,
- Deionised water, and
- Calibration solutions and containers.

pH references

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5.10.2 Redox potential (Eh)

Redox potential gives a measure of the degree of oxidising or reducing conditions in a groundwater system. It is thus also referred to as Oxidation-Reduction Potential (ORP). Oxidation and reduction (redox) reactions involve the transfer of one or more electrons between chemical elements that can exist in more than one oxidation state (called multivalent elements). Redox reactions exert important control on the distribution of species like O_2, NO_3^-, Fe, Mn, SO_4^{2-}, H_2S and CH_4 in groundwater systems. Since many redox reactions are catalysed by micro-organisms, redox potential also affects microbiological activity in groundwater. Thus, redox potential influences the fate and transport of metals and the degradation of organic contaminants (Appelo and Postma 1996).

In a redox reaction, every loss of an electron (oxidation half reaction) is coupled to an electron gain by another species (reduction half reaction). Unlike protons, electrons cannot exist in free or solvated (surrounded by water molecules) form in aqueous solution. Redox potential does not measure the concentration of electrons in solution, but rather the "intensity" of electron transfer. Positive values of Eh indicate more oxidised environments, negative more reduced conditions. Redox equilibria in solution are governed by the Nernst equation (Equation 3). Nernst's equation is theoretically used to calculate Eh from the activities of the dissolved redox active species.

$$E_m = E_o - \left(\frac{RT}{nF}\right) \ln\left(\frac{[\mathrm{ox}]}{\mathrm{red}}\right)$$

Equation 3

Where: E_m is the potential from the ORP electrode (Volts), E_o is related to the potential of the reference electrode, n is the number of electrons in the half reaction, F is Faraday's constant (96.42 kJ/Volt gram equivalent) R is the Gas Law constant (8.314 x 10-3 kJ/mol.deg Kelvin) and T is the temperature (in degrees Kelvin = °C + 273.15).

For detailed discussions of the theory and significance of the electrode approach to redox measurement and groundwater redox measurements read Whitfield (1974), Lindberg and Runnells (1984), Hostettler (1984), Thorstenson (1984), Stumm and Morgan (1996) or Appelo and Postma (1996), Nordström and Wilde (2005).

Redox potential measurement

An electrometric method is used to measure Eh. Electro-active oxidised or reduced species in solution donate or accept electrons from a redox electrode (usually a platinum electrode), creating a potential difference between the redox electrode and a reference electrode immersed in the same solution. Ideally, at redox equilibrium the potential difference between the two electrodes, read from a millivolt meter, is equal to the redox potential (Eh) of the system. Reference solutions with known Eh at a particular temperature are used to check the accuracy of the Eh electrode system.

Eh equipment

Eh measurements require a high impedance potentiometer that can be read in millivolt. A pH meter with added millivolt reading capability can double as an Eh meter. The meter should have a scale readable to ± 1400 mV, with a sensitivity of 0.1 mV. An instrument with temperature probe and automatic temperature compensation would be an advantage. An electrometric Eh measuring system consists of the following:

- Redox potential meter,
- Measuring electrode,
- Flow cell if you're purging,
- Operating manual,
- Reference electrode,
- Redox potential reference solution(s), and
- Extra batteries for the meter.

The measuring electrode and reference electrode may be combined into one combination electrode or Eh probe. Redox potential is temperature dependent, so a means of measuring the temperature is also required.

Redox field measurements

Redox potential measurements are sensitive to reactions of dissolved gases and the use of an airtight flow through cell is essential. Groundwater samples cannot be preserved for Eh measurements and the readings *must* be taken *immediately* in the field. Use an electrode system that has been calibrated and tested for adequate performance. It is difficult to give a stepwise guide on field measurements, refer to the operator's manual as the best guide.

> ***Some natural groundwater*** *does not contain enough electro-active species to give a stable Eh reading even with a flow-through cell. For these poorly poised systems, the Eh reading is generally of little value as a quantitative measurement and the value of the measurement probably does not warrant spending hours waiting for the reading to stabilise.*

Redox potential references

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5.10.3 Electrical conductivity (EC)

Electrical conductivity (EC) is the ability of an aqueous solution to conduct an electric current. The EC of water is measured as the reciprocal of the resistance measured between two parallel metal plates through an aqueous solution at a specified temperature. The EC of water depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Solutions of most inorganic acids, bases, and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution are poor conductors, if at all (APHA, 1998). Electrical conductivity therefore provides gives good measure of the inorganic chemistry quality of the groundwater. The EC is also used for evaluating if the purged groundwater is now representative of water in the aquifer prior to sample collection.

Equipment for conductivity determination

1. Electrical conductivity meter (See that the meter's measurement range suits the site conditions),
2. Calibration solutions,
3. Meter's operator manual,
4. Thermometer, if EC meter is not temperature compensated (See operator manual)

5. Flow cell if you're purging, and

6. Deionised water.

Practical meters and electrodes measure and record the "conductivity" of the water sample. The International System of Unit (SI), which is used by South Africa and most countries, reports conductivity in millisiemens per metre (mS/m). In many other countries the unit of measurement is micromhos per centimetre (µmhos/cm). Some instruments have various scales of sensitivity and unfortunately have named these scales in various fashions such as millisiemens per centimetre or microsiemens per centimetre. Use conversion factors give in Table 18 to change from one-unit to the other.

Table 18 Conversion factors for EC units

1 Siemen per cm (S/cm)	x	100 000	=	1 millisiemen per metre
1 Millisiemen per cm (mS/cm)	x	100	=	1 millisiemen per metre
1 Microsiemen per cm (µS/cm)	x	0.1	=	1 millisiemen per metre
1 Micromho per cm (µmho/cm)	x	0.1	=	1 millisiemen per metre

FEC field measurements

An FEC value that is markedly different from values obtained in nearby boreholes may indicate a different source of water, such as induced recharge, contamination from the surface, or leakage from a formation that contains water of a different quality. Detection of an anomaly may indicate that more detailed sampling or re-evaluation of the borehole is required. If so, the work can usually be done more economically at the time the original sample is collected rather than several weeks or months later.

The EC of a sample can change with time owing to the precipitation of minerals from the water once the sample is in the environment of the container. A sample that has been acidified or otherwise treated will not yield an accurate representation of the EC of the water in the aquifer. It is therefore best to obtain representative EC measurements in the field on fresh water.

Electrical conductivity references

APHA (1998) Standard Methods for the Examination of Water and Wastewater (20th Ed), Am. Public Health Assoc, Washington DC.

Wood, W.W. 1981. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents. Techniques of Water Resources Investigation, Chapter D2, US Geological Survey.

5.10.4 Dissolved oxygen (DO)

Dissolved oxygen is the amount of oxygen dissolved in the water. Recharge is the main source of oxygen in the groundwater. Many chemical and biological reactions in the groundwater are dependent on the amount of oxygen (Domenico and Schwartz 1998). For these reasons, the measurement of DO is important for groundwater quality investigations and especially so when dealing with polluted water. The amount of DO in the water directly influences the ORP (Eh). Less DO equates to low ORP, more DO results in high ORP.

Dissolved oxygen measurements are usually reported as concentration in mg/L (=ppm) which is an actual concentration. Some geochemists prefer to use µmole/L (=0.032 mg/L). For various applications where water is in contact with air, it is more appropriate to express DO as % saturation with respect to air which is a derived unit. The conversion between mg/L and % saturation is described below.

Equipment for DO measurement

It is quite easy to introduce air (and oxygen) in water and therefore only some methods of collecting the water sample for DO testing from the borehole are suitable (Table 19). The rule is that no air should come in contact the sample and the least amount of suction to be applied to lift the sample to the surface. The better pumping methods are therefore all positive displacement devices. The method of choice is a bladder pump, which is also the method of choice for sample collection at pollution sites.

Table 19 Suitability of sampling method or equipment for field measuring of dissolved oxygen

Sampling method or equipment	Acceptability of method	Comment
Bladder pump	Acceptable	Offers flexibility to select sampling depths
Nitrogen displacement	Conditionally acceptable	May cause pressure changes
Gas driven piston pump	Conditionally acceptable	May cause pressure changes
Production borehole (pump in place) pumping	Conditionally acceptable as a method of last resort	Intake level should be borehole below the pumping water level; turbulence and pressure changes can result. Will depend on the pumping rate
Low flow purging	Acceptable	Intake level should be borehole below the water level; turbulence and pressure changes can result
Bailer	Unacceptable	Transfer of sample can affect dissolved gases
Suction lift (centrifugal) pump	Unacceptable	Outgassing (loss of oxygen) is likely to occur
Airlift pump	Unacceptable	Oxygenation of the sample will occur

(Source: Rose and Long 1988)

Checklist of dissolved oxygen equipment:

- DO meter and electrode (with spare membranes, O-rings and electrolyte)
- Flow-through cell, important to prevent influence of air
- Thermometer (if not included in the DO meter)
- Barometer (if not included in the DO meter)
- At least two 250 mL plastic bottles
- One 1000 mL plastic bottle for aeration of reference sample or manufacturer's aeration flask.
- Zero DO solution: dissolve 12g sodium sulphite (Na_2SO_3) and a few crystals of cobaltous chloride ($CoCl_2$) in 100 ml of deionised water. This is used to make up a zero DO solution. Prepare a fresh solution for each sample trip.

Dissolved oxygen measurement

Actual DO measurement of the sample water should be done once the meter/electrode system has been calibrated. *Calibrate the DO meter according to the manufacturer's instruction*s. The analysis procedure with a calibrated system is as follows:

- Place the calibrated sensor in the flow-through cell. Gently open the flow control valve.
- Measure the DO concentration at about 5-10 minute intervals until a stable reading is obtained. Do not change the pressure or temperature dial on the meter after calibration. Low flow rate is ideal.
- Record the meter reading to the nearest 0.1 mg/L
- Make another measurement to replicate the results.
- Dismantle and wash the equipment with distilled water.
- Store the electrode according to the manufacturer's instructions. This usually means that the membrane tip of the electrode needs to be kept moist.

Measure the dissolved oxygen *in a flowing stream of water and NEVER use discrete samples.*

Suitability of pumps for DO monitoring

When sampling for DO, the rule is that no air should contact the sample and the least amount of suction should be applied to lift the sample to the surface. The better pumping methods are therefore all positive displacement devices. The method of choice is a bladder pump, which is also the method of choice for sample collection at pollution sites. The guide by Rose and Long (1988) can help you to decide on the suitability of devices or sampling method to collect samples for DO analysis/monitoring (Table 20).

Table 20 Sampling pumps suitable for monitoring dissolved oxygen

Sampling method or recovery mechanism	Acceptability of method	Comment
Bladder pump	Acceptable	Offers flexibility to select sampling depths
Nitrogen displacement	Conditionally acceptable	May cause pressure changes
Gas driven piston pump	Conditionally acceptable	May cause pressure changes
Natural spring	Conditionally acceptable	Sampling bottle should be held borehole below the spring orifice
Production borehole (pump in place) pumping	Conditionally acceptable as a method of last resort	Intake level should be borehole below the pumping water level; turbulence and pressure changes can result.
Portable submersible pump	Conditionally acceptable as a method of last resort	Intake level should be borehole below the water level; turbulence and pressure changes can result.
Bailer	Unacceptable	Transfer of sample can disturb dissolved gases
Suction lift (centrifugal) pump	Unacceptable	Outgassing (loss of oxygen) is likely to occur
Airlift pump	Unacceptable	Oxygenation of the sample will occur

Dissolved oxygen references

APHA 1998. Standard Methods for the Examination of Water and Wastewater (20th ed), Am. Public Health Assoc., Washington DC.

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Domenico, P.A, and Schwartz, F.W. 1998. Physical and Chemical Hydrogeology (2nd ed), John Wiley & Sons, New York, 505p.

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Stumm, W. and J.J. Morgan 1996. Aquatic chemistry (3rd ed), John Wiley & Sons, New York.

Weiss, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. Deep-Sea Research 17, 721-735.

White, A F, Peterson, M.L. and Solbau, R.D. 1990. Measurement and interpretation of low levels of dissolved oxygen in ground water. Ground Water 28(4) 584-590.

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5.10.5 Alkalinity and acidity

Alkalinity

Alkalinity of water measures its acid neutralising capacity. Alkalinity consists of the sum of titratable carbonate and non-carbonate chemical species in a filtered water sample as influenced by the pH of a sample. For most groundwater with pH between 6 and 8, total alkalinity essentially represents the bicarbonate concentration. For this reason, alkalinity titration with acid is used to approximate bicarbonate levels in order to complete the ion balance of water samples. High levels of borates, phosphates and silicates can also contribute to alkalinity and in such cases suitable adjustments have to be made to achieve proper ion balance.

If the investigation requires an understanding of the chemical equilibrium related to carbonate minerals, it is essential to obtain accurate values of pH, carbonate and bicarbonate concentrations of the groundwater. In such cases, you should conduct a total alkalinity determination (titration) in the field, or else, measure the pH during sample collection and analyse the sample in a laboratory on the same day. This last procedure is recommended and of course it makes the task of the field sampler easier. In many cases, particularly where there are substantial quantities of free CO_2 involved, it is better to do alkalinity determinations right in the field at the borehole on a fresh sample.

Measure alkalinity in the field *if it is a critical determinant for the investigation or monitoring program. However, for most purposes alkalinity is sufficiently stable that it can be measured in the laboratory.*

Alkalinity equipment

1. pH meter, buffers and glassware for pH measurement,
2. 25 mL burette,

3. 25 or 50 mL pipette,
4. magnetic stirrer and stirrer bar,
5. Stands, clamps and beakers,
6. Hydrochloric acid 0.01 to 0.1M,
7. Sodium hydroxide solution 0.01 to 0.1M (only for acidity determination)
8. Distilled or deionised water, and
9. Borehole-padded storage box to prevent breakage of glassware.

Various concentrations of acid/alkali can be used for the titration, as long as the concentration is known accurately. Use either standard hydrochloric acid solutions of certified concentration or ask the lab to standardise the solution. For high alkalinity samples, titrations will be quicker with a more concentrated acid (e.g. 0.1M). For low alkalinity samples, a more dilute acid (e.g. 0.02M) will give more accurate results.

This equipment is not easily obtained off-the-shelf. If you intend to conduct such an investigation and need to titrate in the field, acquire the necessary equipment and be sure to carry out a sufficient number of titrations in the laboratory under supervision before doing them in the field. Conducting field alkalinity titrations is not difficult: do not be put off by the apparent complexity, but do stick to the rules.

Alkalinity measurement equipment

There is three types of alkalinity measurement equipment; burette, micrometer burette, and digital titrator. Visit Wilde (variously dated) for more details about this equipment. Burette alkalinity measurement equipment is presented in this manual as it is fairly basic equipment.

Burette alkalinity titration

The titration procedure to determine alkalinity is as follows:

1. Set up the burette, pH meter and magnetic stirrer.
2. Calibrate the pH meter with buffers according to the to manufacturer's instruction.
3. Rinse the burette with a small quantity of acid (of molarity M_1).
4. Rinse a beaker and stirrer bar with distilled/deionized water.
5. Rinse the pipette with sample water and transfer a measured volume (V_2) of sample to the beaker.
6. Insert the pH sensor in the solution, start the stirrer and monitor the pH. Ensure that the stirrer mixes the water gently and does not touch the pH sensor.

7. Record the pH when a stable value has been reached.
8. If the pH of the water is greater than 9, a two-point titration will be required. In that case, follow step 9 to 13 to the end point at pH 8 and the repeat the same steps to end point pH 4.
9. Add a small quantity of acid to the solution, note the burette reading (V) and record the pH value when it has reached stability.
10. Repeat step 9 until the pH is below 3.
11. Plot out the pH as function of the volume of acid added (Figure 10).
12. Determine the end point (V_1) by one of two methods:
    a. Visually establish the value of V at which the pH changed most rapidly,
    b. A more precise alternative to (13) is to calculate the slope $(= \Delta pH/\Delta V)$ for each interval, plot it against V (Figure 10) and determine the points of maximum slope,
13. The calculation of alkalinity is done using the following equation:

$$Alk = M_1 \, x \, \frac{V_1}{V_2} x \; 1000 \; x \; 50 \; (in \; mg \; CaCO_3/L)$$

Equation 4

14. Rinse the beaker and pipette. Discard unused acid from the burette and pack everything away.

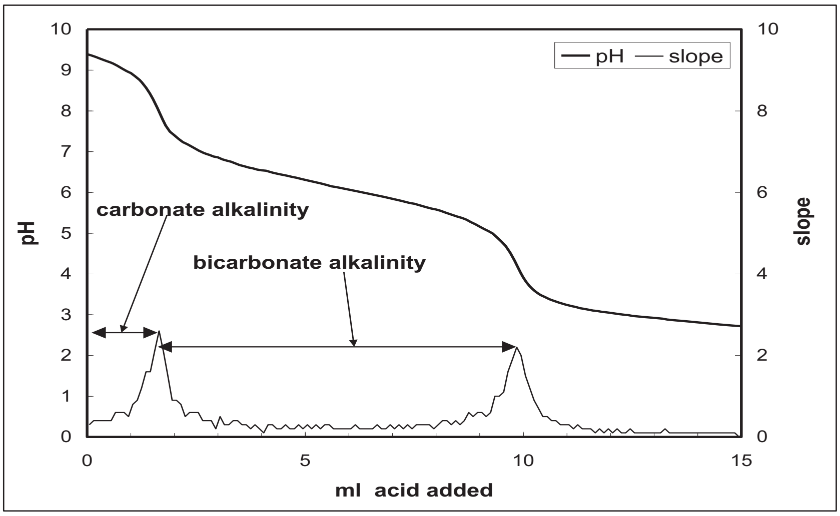

Figure 10 Typical titration curve of a somewhat alkaline, unpolluted water sample. The upper curve shows the pH change as function of quantity of acid added. The lower curve shows the calculated slope $(= \Delta pH/\Delta V)$

EXAMPLE

100 ml (V_2) sample was titrated with 0.1M HCl (M1). The first endpoint was at 0.8 ml acid, the second endpoint at a burette reading of 8 ml acid. What are the different alkalinity values?

Use the equation $A = M_1 \times V_1/V_2 \times 1000 \times 50$

For the first endpoint, $V_1=0.8$ *ml, from which*

Carbonate alkalinity: $A_c = 0.1 x 0.8 / 100 x 1000 x 50 = 40$ *mg* $CaCO_3/L$

The second end-point (V_1) *is* $8 – 0.8 = 7.2$ *ml. Then*

Bicarbonate alkalinity: $A_b = 0.1 x 7.2 / 100 x 1000 x 50 = 360$ *mg* $CaCO_3/L$

Therefore Total alkalinity: $TA = A_c + A_b = 40 + 360 = 400$ *mg* $CaCO_3/L$

If we know that there are no other bases present, then the carbonate content will be
$[CO_3^{2-}] = 40$ *mg* $CaCO_3/L = 40 x 30 / 50 = 24$ *mg* CO_3/L *and*

$[HCO_3^-] = 360$ *mg* $CaCO_3/L = 360 x 61 / 50 = 439$ *mg* HCO_3/L

In some field conditions it may be difficult to work with a burette, retort stand and stirrer. An alternative method is to use two or more pipettes of different volume (auto-pipettes are easiest) to deliver the acid.

Acidity titration

The titration for acidity is usually done with sodium hydroxide solution following the same procedure. The special requirement of sodium hydroxide solution is that it can absorb CO_2. Keep the bottle stoppered and discard used solution from the burette. The pH endpoint is selected to fit the nature of the acid producing compounds in the water. In natural waters where, dissolved CO_2 is the only acid present, titration is carried to pH 8.3 and reflects the amount of CO_2 dissolved in the water. In polluted waters, the required endpoint may be different. A general practice is to titrate to pH of 3.7 (methyl orange endpoint) and then to pH 8.3 (phenolphthalein endpoint) (APHA 1998: method 2310B). Results should be reported as "acidity to pH……" and can be expressed in $mgCaCO_3/L$ or meq/L. Unpolluted water with high CO_2 content (low pH) needs to be handled with care to minimize CO_2 loss.

Alkalinity and acidity units

Alkalinity and acidity concentrations are usually reported as $mgCaCO_3/L$. This is an equivalent unit and equates all the contributors of the alkalinity as if they were $CaCO_3$ (which they usually are not). This unit has developed in the water treatment industry and has become standard in the South African water supply industry. The other equivalent unit is milli-equivalent/litre (meq/L) which is more popular amongst chemists. In other countries, measured alkalinity results are reported as the individual bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) components. Carbonate is determined from the first endpoint and bicarbonate from the second endpoint (Figure 10). The conversion formulae are as follows:

$$1\ meq\ alkalinity = 50\ mgCaCO_3 = 61\ mgHCO_3^- = 30\ mgHCO_3^{2-}$$

Some databases and chemical modelling software programs require the input of bicarbonate and carbonate species separately as mg/L rather than the analysed alkalinity. If the field pH of unpolluted water is below pH 8.0, the carbonate concentration is negligible and the alkalinity can be taken as the bicarbonate concentration using the conversion factors above. For alkaline waters (pH>8), the alkalinity titration should be carried out to two end points. The amount of acid added to reach the first end point (nominally pH 8.3) gives an approximation of the carbonate concentration and the second endpoint (nominally pH 4.5) approximates the bicarbonate concentration.

References - Alkalinity and acidity

APHA 1998. Standard Methods for the Examination of Water and Wastewater (20th ed), Am Public Health Assoc, Washington DC.

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Rounds, S.A. 2006. Alkalinity and acid neutralizing capacity (version 3.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.6. Available from the URL: http://pubs.water.usgs.gov/twri9A6/ (last accessed on 5 November 2006).

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Wilde, F.D., ed., variously dated, Field Measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, accessed from http://pubs.water.usgs.gov/twri9A/ on 10 October 2016.

5.10.6 Filtration

It is important to understand the motive for filtration, when and how to filter. Just like many of the groundwater sampling field procedures, consideration for filtration is also depended on the goals of sampling and site hydrogeology conditions among other factors.

High particle sediment (turbidity) loadings might lead to significant analytical bias through inclusion of large quantities of matrix metals in the analysis because acidification dissolves precipitates or causes adsorbed metals to desorb. Groundwater samples for the analysis of metals (trace elements and toxic metals including mercury) are acidified to prevent the adsorption of metals onto the walls of the container and keep them dissolved in solution thus preventing precipitation. Metal ions could also be removed from solution during shipment and storage as a result of interactions with particle surfaces. Prior to acidification, groundwater samples for the analysis of metals must be filtered.

Main causes of high turbidity:

- Low permeable/yield aquifers – can result in limited natural replenishment to flush the sediments, but also excessive drawdown could be induced during purging leading to turbulent flow which can mobilise formation sediments close to the borehole,
- Poor borehole development - causes load of sediments and other particle matter from drilling to remain in the borehole, and
- Sample collection methods - high purging rates tend to create turbulent flow and mobilisation of sediments while bailers can also collect stagnant which might also be high in turbidity. Low-flow sampling when done properly would reduce the mobilisation of formation sediments leading to low turbidity and reduced need for filtration.

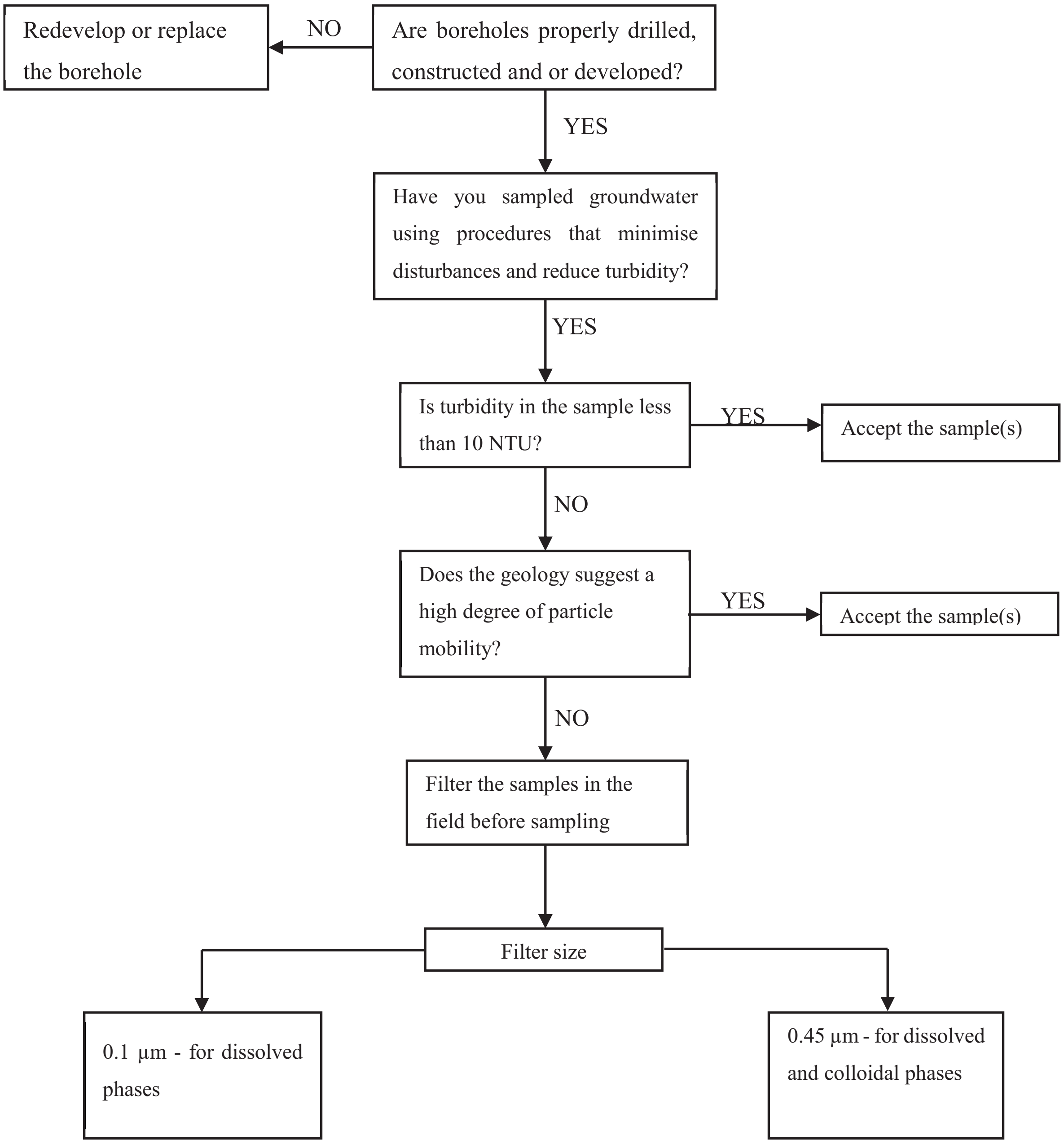
Filtration aspects and procedures *for groundwater samples are comprehensively discussed by Braids et al. 1987; Plus and Barcelona 1996 and Saar 1997.*

Considerations for groundwater sample filtration

The question as to whether or not to filter the sample before analysis to some extent depends on the original question posed at the start of your groundwater sampling program, “What is the purpose of the sampling program?” As noted a few times in this manual, the purpose of the monitoring influences the contents of the monitoring programme which, in turn, prescribes the sampling procedures. In some cases, collection of both filtered and unfiltered samples might be important for comparison purposes. This is particularly important at the start of a sampling programme. Unfiltered data could be more preferable for a risk assessment of the drinking water pathway as the worst-case scenario (U.S. EPA, 1991), but for drinking water quality assessment purposes, filtered samples better resemble the state that groundwater at consumption.

Groundwater samples brought to the surface will to varying degrees, contain dissolved species, colloids and suspended particles. The truly dissolved phase has molecules or polymers that are much smaller than 0.1 micron (1 micron = 1 µm). Colloids range in size from 0.1 µm to 10 µm (Puls and Barcelona 1996, Saar 1987) while suspended particles are larger. Filters come in a variety of filter pore sizes, commonly ranging from 0.1 µm to 5 µm. Thus, depending on the filter size used, you can filter out some or most of the colloids and the suspended particles. The boundary between the particulate and dissolved species is operationally defined at a filter size of 0.45 µm (Karl et al. 1994). The boundary implies that the component retained and those passing through a 0.45 µm filter represents suspended solids and dissolved metals respectively.

The Ohio Environmental Protection Agency (2012) suggests the use of a groundwater sampling field filtration decision tree (Figure 11) when making filtration considerations.



Source: Modified from Ohio Environmental Protection Agency (2012)

Figure 11 Groundwater sampling field filtration decision tree

Filtration methods

Table **21** shows a summary of the main filtration methods, their attributes and applicability (Ohio Environmental Protection Agency 2012).

Table 21 Summary of the main filtration methods, their attributes and applicability

Filtration methods	Attributes and applicability
In-line filtering	- Utilise positive pressure generated by the sampling pump - Should be used wherever possible - Closed and isolated from atmospheric influences on the sample - Only suitable for low flow purging
Off-line filtering	- Samples has to be transferred to filtration system - Increases of potential of exposure to atmospheric influences - Suitable for both bailering and purging - Filtration has to be done immediately after sampling to prevent alteration chemistry in the sample - Range of tools on the market widely varies their but mainly driving mechanism is either vacuum or pressure - Vacuum systems less preferable as they can cause degassing of sample and influence metal concentrations (Barcelona et al. 1985)

Sources: Sundaram et al. 2009 and Ohio Environmental Protection Agency (2012)

In terms of filtering materials, NCASI (1982); Ohio Environmental Protection Agency (2012) recommends the use of polycarbonate or cellulose acetate filter. Cellulose membranes and glass microfiber filters are commonly used.

Filtration procedures

Filtration procedure will vary from one piece of equipment/method to another. One must therefore make good use of the manufacturer's instructions for both operation and maintenance of the filtration equipment and or devices. A general procedure that could be helpful is presented here.

1. Insert the filter membrane to the holder (equipment) correct side up, usually the side with the printed grid.
2. Pre-rinse the filters following manufacturer's recommendations to remove the residue from the manufacturing, packing, or handling.
3. Connect the in-line filter to the discharge pipe, or draw up a sample into the pressure-filter.
4. Flushing the system by discard the first 50 mL.
5. Collect the required amount of filtered sample.

6. Discard filter membrane (and also Syringe if it has been used), or in-line filter, in a waste-bag: do not litter.
7. Disassemble filter apparatus and rinse clean with deionised water.
8. Make sure the filtering procedure is properly described in the sampling programme, and is adhered to for all sampling runs.

Filtration references

Barcelona, M. J., J. P. Gibb, J. A. Helfrich, and E. E. Garske. 1985. Practical Guide for Ground-Water Sampling. Illinois State Water Survey. Champaign, Illinois. Contract Report 374.

Braids OC, Burger RM and Trela JJ (1987). Should groundwater samples from monitoring boreholes be filtered before laboratory analysis?

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5.10.7 Sample preparation, containers, preservation and storage

It is critical that the composition of the sample submitted to the laboratory be representative of the water source you are evaluating. Sample composition is affected soon after the sample is taken. The way the sample is handled, stored, and transported to the laboratory is directly related to the quality of the results delivered. Depending on the analyte of concern, the action of microbes, aeration, temperature, and chemical reactivity may affect the chemical makeup of the sample. Therefore, appropriate and effective sample preservation is critical in minimising these effects prior to analysis.

Always consult the analytical laboratory about the volume of sample required and advice on container types and if there any specific preservation they require or recommend. Some laboratories, do have these sampling containers which you can purchase. Summarised information about sample container types, preparation, preservation and storage samples is presented as follows:

- Table 22: inorganic chemistry determinants (Weaver et al. 2007; Sundaram et al. 2009; Ohio Environmental Protection Agency 2012),
-
- Table **23**: common organic related determinants (Sundaram et al. 2009; Ohio Environmental Protection Agency 2012),
- Table 24: Other determinants, and
- Table 25: microbiological determinants (U.S. EPA 2015).

Table 22 Information on sample container types, preparation, preservation and storage samples for the analysis of inorganic chemistry determinants

INORGANIC CHEMISTRY DETERMINANTS				
DETERMINANT	**CONTAINER**	**PREPARATION**	**PRESERVATION**	**MAXIMUM** HOLDING TIME**
Major ions	P or G	Filter if phosphate is a critical determinant	Cool storage (0-6 ^{0}C)	28 days
Acidity	P or G	NSP	Cool storage (0-6 ^{0}C)	14 days
	P or G	NSP	Cool storage (0-6 ^{0}C)	14 days
Ammonia	P or G	NSP	Cool storage, 0-6 oC; H_2SO_4 to pH<2	28 days
Ammonium	P or G			
Bromide	P or G	NSP	NR	28 days*
Chloride	P or G	NSP	NR	28 days*
Chlorine	P or G	NSP	NR	Analyse immediately (within 15 minutes
Cyanide, total	P or G	NSP	Cool storage 0-6^{0}C; add NaOH to pH>12 ascorbic acid if	14 days

			oxidants (e.g., Chlorine is present.)	
Hardness	P or G	NSP	HNO_3 to pH<2; H_2SO_4 to pH<2	6 months
Fluoride and Iodide	Brown glass bottle	NSP	Cool storage, 0-6 ^{0}C	28 days*
Kjeldahl and organic nitrogen	P or G	NSP	Cool storage, 0-6 ^{0}C; H_2SO_4 to pH<2	
Nitrate	P or G	NSP	Cool storage (0-6 ^{0}C)	48 hours
Nitrate-nitrite	P or G	NSP	Cool storage, 0-6 ^{0}C; add H_2SO_4 to pH<2	28 days
Sulphate	P or G	NSP	Cool storage (0-6 ^{0}C)	28 days
Sulphide	P or G	NSP	Cool, 0-6 ^{0}C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulphite	P or G	NSP	NR	Analyse within 15 minutes
Metals (not inclusive of Cr(VI) & Hg)	P or G	Filter through 0.45 µm membrane filter (Consider Figure 11)	HNO_3 to pH<2 at least 24 hours prior to analysis, Cool storage (0-6 ^{0}C)	6 months
Chromium (Cr) VI	P or G	Filter through 0.45 µm membrane filter (Consider Figure 11	Cool storage (0-6 ^{0}C)	24 hours
Chromium (Cr) VI	P or G	Filter through 0.45 µm membrane filter (Consider Figure 11)	Add sodium hydroxide and ammonium sulphate buffer solution to pH 9.3 to 9.7 to extend holding time to 28 days, Cool storage (0-6 ^{0}C)	28 days
Mercury (Hg)	P or G	Filter through 0.45 µm membrane filter (Consider Figure 11)	HNO_3 to pH<2 Cool storage (0-6 ^{0}C)	28 days
	P or G			
Nutrients (e.g. phosphates)	P or G	Filter through 0.45 µm membrane filter	Freeze	28 days
Fluoride and Iodide	P or G	NR	NR	28 days

NSP - No Special Preparation; P - Polyethylene; G – Glass

* The preservative and holding times may vary with sampling procedures, method analysis and selected laboratory

**Maximum holding time includes waiting time in the laboratory

Sources: Sundaram et al. 2009; Ohio Environmental Protection Agency 2012.

Table 23 Summarised information on sample container types, preparation, preservation and storage of samples for common organic related determinants

DETERMINANT	CONTAINER	PREPARATION	PRESERVATION	MAXIMUM* HOLDING TIME
Volatiles	Glass, Teflon-lined cap	NSP	Cool storage, 0-6 ^{0}C; 0.008% $Na_2S_2O_3$; HCl to pH<2, Ensure no head space in the sample	14 days
Acrolein and acrylonitrile	Glass, Teflon-lined cap	NSP	Cool storage, 0-6 ^{0}C; 0.008% $Na_2S_2O_3$, adjust pH to 4-5	14 days
Dioxins and Furans	Glass, Teflon-lined cap	NSP	Cool storage, 0-6 ^{0}C	30 days until extraction, 45 days after extraction
Oil and grease	Glass	NSP	Cool storage, 0-6oC; H_2SO4 or HCl to pH<2	28 days
Phenols	Glass, Teflon-lined cap	NSP	$Na_2S_2O_3$	7 days until extraction, 40 days after extraction
PCBs	Glass, Teflon-lined cap	NSP	Cool storage, 0-6^{0}C	1 year
Pesticides	Glass, Teflon-lined cap	NSP	Cool storage, 0-6^{0}C; pH 5-9	1 year

*The preservative and holding times may vary with sampling procedures, method analysis and selected laboratory

Sources: Sundaram et al. 2009; Ohio Environmental Protection Agency (2012)

Table 24 Summarised information on sample container types, preparation, preservation and storage of samples for other common determinants

DETERMINANT	CONTAINER	PREPARATION	PRESERVATION	MAXIMUM** HOLDING TIME
Radiological Alpha, beta, and radium	Glass, Teflon-lined cap	NSP	HNO_3 to pH<2	6 months

Radioactive Isotope-Tritium	Glass, Teflon-lined cap	Fill bottle directly from pump discharge hose. Leave 1 cm air-gap for expansion	Cool storage, 0-6^{0}C	*
Dissolved gasses	Non-permeable bottle, Gas bags, flask	Fill according to instruction	Cool storage, 0-6^{0}C	*
Stable Isotopes-Deuterium, Oxygen in water	P or G with tightly fitting caps.	Fill to the top and ensure no air bubbles, seal tightly	Cool storage, 0-6^{0}C	*
Stable Isotopes-Sulphur, Oxygen in Sulphate	High Density Polyethylene (HDPE) bottle	Filter through 0.45 µm membrane filter	Add 1-2 mL of acid (HNO_3, HCl), shake and let react, then add 10 g barium chloride to precipitate barium sulphate.	*
Nitrogen-15	P or G with tightly fitting caps.	Fill to the top and ensure no air bubbles, seal tightly	Treat samples with acid, chloroform, HCl or Hg_2Cl_2 (consult the laboratory) or freezing the sample, Cool storage, 0-6^{0}C	*
Carbon-14	Brown glass	NSP	Keep samples cool and in the dark. If biological activity is expected, preservation (with NaN_2 or $HgCl_2$**) is required.	*
Chlorine-36	Brown glass	Filter through 0.45 µm membrane filter (Consider Figure 11)	Cool storage in dark, 0-6^{0}C	*

*Could not be found from literature, Note that $HgCl_2$ is poisonous and should be avoided when possible.

Sources: Sundaram et al. 2009; Ohio Environmental Protection Agency (2012)

Table 25 Summarised information on sample container types, preparation, preservation and storage of samples for common microbiological determinants

MICROBIOLOGICAL DETERMINANTS	CONTAINER	PREPARATION	PRESERVATION	MAXIMUM HOLDING TIME
Total coliforms; Faecal coliforms; E. coli; Enterococci; Heterotrophic Bacteria; or Coliphage	125 or 150 mL plastic bottles	Sterilise the bottles, don't filter	Add sodium thiosulfate if sample is chlorinated and cool storage 0-6^{0}C, make sure they don't freeze	8 hours for compliance samples, 30 hours for drinking water samples, 48 hours

				for coliphage samples
Giardia and Cryptosporidium	Plastic cubitainers or equivalent	Sterilize the bottles	Cool storage 0-6^{0}C, make sure they don't freeze	96 hours

Source: U.S. EPA (2015)

References - sample reservation

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5.10.8 Equipment decontamination

All equipment that comes in contact with the sample should be cleaned before sampling from the next hole to prevent cross contamination. Obtaining erroneous results through cross contamination of boreholes is unforgivable because groundwater sampling is an expensive exercise in terms of both time and money.

Following a few simple steps given in section reduce potential errors of cross contamination. If, however, a monitoring programme is designed where the possibility of cross contamination of samples and boreholes is critical to the credibility of chemical data, the decontamination routine becomes more stringent and structured. The degree of stringency of decontamination procedure is dependent on the nature and level of suspected or known contaminants and project aims/requirements. Decontamination procedure would also depend on the nature and levels of contaminants at hand. For detailed information on decontamination, visit the references given at the end of this section chapter. A general decision tree table to guide the selection of decontamination procedures when sampling groundwater is presented in

Table **26**.

Table 26 A general decision tree table to guide the selection of decontamination procedures

Which analysis are you sampling for?	Decontamination procedure
Drinking, domestic or irrigation quality	1. Thoroughly rinse with phosphate free detergent solution 2. Rinse with portable water 3. Air dry before use
Metals	1. Rinse with 10% hydrochloric or nitric acid (Caution: Dilute HNO3 may oxidize stainless steel, rinse only non-metallic surfaces) 2. Deionized/distilled water final rinse 3. Air dry before use
Organics (inclusive of gases)	1. Rinse with solvent-pesticide grade isopropanol, acetone, or methanol, alone or in some combination (*Solvent must not be an analyte of interest*). 2. Deionized/distilled water Final rinse 3. Air dry before use

At highly contaminated or sensitive sites, the following type of cleaning is recommended (Parker and Ranney 1997a, 1997b):

- Stainless steel and PVC – clean using a hot detergent wash,
- PTFE, LDPE, and the more adsorptive polymers - hot detergent wash plus drying in a hot oven

Words of advice on decontamination and cross-contamination

- *Minimise the effects of cross-contamination by starting to sample from the least contaminated boreholes then progressing to the more contaminated one,*
- *Use sampling equipment that is easy to clean and pumps that can easily be disassemble,*
- *Dispose of the purged water appropriately to prevent cross-contamination but also impacting negatively on the environment, and*

- *Take measures to avoid the decontamination products (or breakdown products) from being introduced into the sample.*

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6 SAMPLING OF DISSOLVED GASES IN GROUNDWATER

6.1 Introduction

Dissolved gases (DG) in groundwater can be naturally occurring, or it may have been artificially introduced through anthropogenic actives and processes. The measurement of dissolved gases (DG) in groundwater has a variety of applications. These applications range from hydrocarbon prospecting, investigations of hydrological and hydrogeological processes (e.g., Aeschbach-Hertig et al. 1999; Wilson and Mackay 1996; Ryan et al. 2000; Blicher-Mathiesen et al. 1998; petroleum hydrocarbon contaminants (e.g., Amos et al. 2005) and remediation (Zhang and Gillham 2005).

The current worldwide boom of 'unconventional' oil, shale gas Underground Coal Gasification (UCG) industry has brought about increased and intense attention to the potential impacts of the oil and gas exploration activities on the groundwater quality. Shale gas is largely composed of methane, but other gas contents such as ethane and propane among others are also of particular concern (Vidic et al. 2013; Vengosh et al. 2014 and Christian et al. 2016). The measurement of DG in groundwater has therefore becoming increasingly important for oil and gas industry operators to establish baseline dissolved hydrocarbon gas concentrations (i.e., primarily methane, but for other minor gas contents) and thereafter for groundwater quality impact assessment (Molofsky et. 2013; Siegel et al. 2015). Dissolution of gas from groundwater can also result in fires and explosions when it enters buildings.

Other potential sources of dissolved gas include: leakage from underground gas storage reservoirs, sanitary landfills, mines and mine spoil and degassing of coal seams, among others. It is therefore important to evaluate groundwater gas concentrations and potential source processes in order to assess their significance for chemical evolution and human safety (Pitkänen and Partamies 2007). Isotopic compositions of gases are very in interpreting the origin and transformation of the gas species. Evaluation of groundwater gas concentrations requires that DG in groundwater is measured. In order to do this, groundwater samples for DG analyses must be properly collected using appropriate sampling methods and devices.

6.2 Methods and equipment for sampling of DG

There are currently two main sampling methods for collection of gases; open system and closed system. In the open system some of the dissolved gases might escape to the atmosphere, whereas a closed system can trap all gases; both dissolved and effervescing (Molofsky et al. 2016). The procedures and guidelines presented here adopted from (Isotech 2014a, Isotech 2014b and Isotech 2014d). At this particular time, Isotech Laboratories, Inc. appears to be main supplier of reputable equipment and devices for the collection of groundwater DG samples.

Open system - direct fill

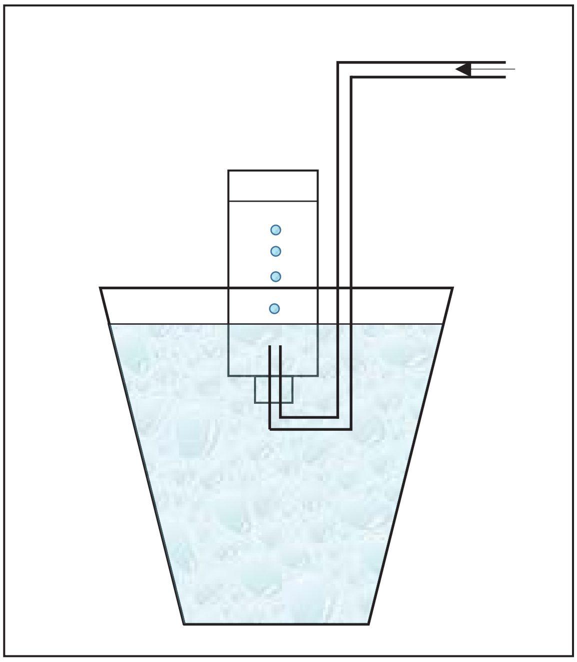
When the dissolved gas in the groundwater is under-saturated, bubbles do not form when the groundwater sample is brought to the surface. A groundwater sample can thus be collected at the surface with minimum loss of the dissolved gas phase through effervescence. The groundwater sample should be collected in non-permeable bottle and care should be taken to minimise contact with air (Isotech 2014). This approach is regarded as an open system as some of the dissolved gases might escape to the atmosphere during the sampling process.

Procedure:

- Set-up the low-flow sampling equipment and purge using the guidance given in the *PRE-SAMPLING PHASE*,
- When sufficient purging has been achieved as indicated by stabilisation of measured field parameters, prepare to collect the samples from the tap outlet,
- Open the non-permeable labelled sampling bottle, rinse it three times with the water to be sampled,
- Collect the sample by filling the bottle completely, close and store (0-6 ºC) or preservation to prevent bacterial activity prior to laboratory analysis,
- For preservation, addition of bactericide to prevent microbial degradation (Hackley 2012).

Semi-closed system - Water displacement - gas phase technique

In the semi-closed system, the sample is not in direct contact with the atmosphere while the water in the bucket is in contact with the atmosphere during sample collection. The DG is groundwater is collected by filling an appropriate sampling bottle while inverted in a bucket filed of purge water (See illustration in Figure 12). The method has long been used to collect DG in groundwater (Meents 1960; Coleman et al. 1988; Hirsche and Mayer 2009; Bolton and Pham 2013; Molofsky et al. 2016).



Source: Hackley et al. (2012)

Figure 12 Schematic of water displacement - gas phase technique showing the DG phase is collected in a semi-closed system

Use the following steps as a guide:

1. Set-up the low-flow sampling equipment and purge using the guidance given in the *PRE-SAMPLING PHASE*.
2. When sufficient purging has been achieved as indicated by stabilisation of measured field parameters, fill a 5L bucket with the purged prepare to collect the samples from the tap outlet.
3. Connect the filling tube to the sampling bottle, invert the bottle and submerge it the filled 5L bucket as shown in Figure 12.
4. While the bottle is inverted, attach the filling tube to a valve connected to borehole purging line.
5. The dissolved gas phase collected will displace the water in the inverted bottle.
6. Close the bottle (still in the same inverted position) when sufficient gas has been collected according to the analytical laboratory's requirements.
7. Cool storage (0-6 °C) to prevent bacterial activity prior to laboratory analysis.

Closed system

When groundwater at depth is supersaturated with gases concentrations above its solubility limit at the surface can be sustained because in the aquifer hydrostatic head pressure is greater than atmosphere pressure. It is however difficult to maintain the hydrostatic pressure as the sample is pumped to the surface. As the pressure decreases the amount of the gas that can be maintained in solution also decreases and in-order to try and maintain equilibrium, gas effervescing (bubbles) occurs. Continued exsolution of the gas would eventually lead to under saturation.

The closed system therefore collects both the water and the gas phase, its main aim is to trap all gases; both dissolved and effervescing phases. This enables adequate measurement of the total gas concentration in that was in the groundwater at sampling depth. The closed system gas collection or sampling method provides the most accurate means for the measurement of DG under all conditions (Molofsky et al. 2016). Under the closed system, there are currently two main methods of collecting DG samples; IsoBags® (gas bags) (Isotech 2014b) and IsoFlask® (Isotech 2014c).

For a closed system remember that:

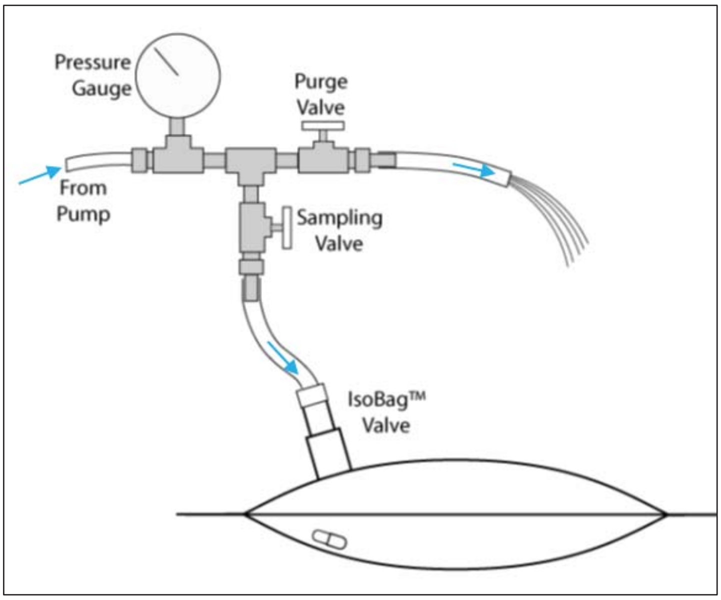
- *Water samples should either be collected from a pressurised water system (by pass treatment unit) or by using suitable water pump.*
- *When a pump used, it should be capable of maintaining a constant pressure at or above that which exists within the aquifer to ensure that gases dissolved in the water within the aquifer remain dissolved until the water is transferred into an or IsoBag®* or *IsoFlask®.*

IsoBags®

These are evacuated bags used to collect groundwater samples supersaturated with DG.

Sample collection unit

The DG collection unit comprise of a pressure gauge attached to the spigot or purging pump output in line with two valves for purging and sampling into the IsoBag® (Figure 13). The outlet of the sampling valve is connected to the IsoBag® through some fittings that are supplied with the unit. The purge valve enables purging of the borehole and the tubing while the sampling valve facilitates bleeding of any air or gas before samples can be collected (Isotech 2014b).



Source: Modified from Isotech (2014b)

Figure 13 Schematic showing the DG collection unit comprising of a pressure gauge attached to the spigot or purging pump outlet in line with two valves for purging and sampling into the IsoBag®

<u>Sample collection procedure (Adopted from Isotech 2014b)</u>

1. Set-up the low-flow sampling equipment and purge.
2. When sufficient purging has been achieved as indicated by stabilisation of measured field parameters, prepare to collect the samples as follows:
    - Attach the DG collection unit to attached to the spigot or purging pump outlet as illustrated in Figure 13,
    - Slowly open the purge valve to purge any gas or air from the tubing,
    - The flow rate should be controlled so as to allow a reasonable flow, while also maintaining a pressure close to the maximum pressure of the water system or pump,
    - Ensure that the line has been adequately purged of any gas or air and allow for a steady state flow to be achieved between collection unit inflow and outflow,
3. Once this is achieved, slightly open the sampling valve to purge (bleed) any gas or air from the sampling line.
4. After bleeding of any gas or air from the sampling line, keep the water running at a low rate.
5. Connect the fitting to the valve on the IsoBag® and then proceed to fill the bag, slower filling rate ensures greater the averaging effect.
6. After sufficient sample has been collected as per manufacturer's instruction, close the sampling valve and quickly disconnect the fitting from the IsoBag.

7. For preservation, store cool (0-6 ºC) or add bactericide to prevent microbial degradation (Hackley et al. 2012).
8. When sampling is completed, stop the pump, disconnect and clean the equipment. If contaminated, follow equipment decontaminated guideline procedures given in
9. Table **26**.

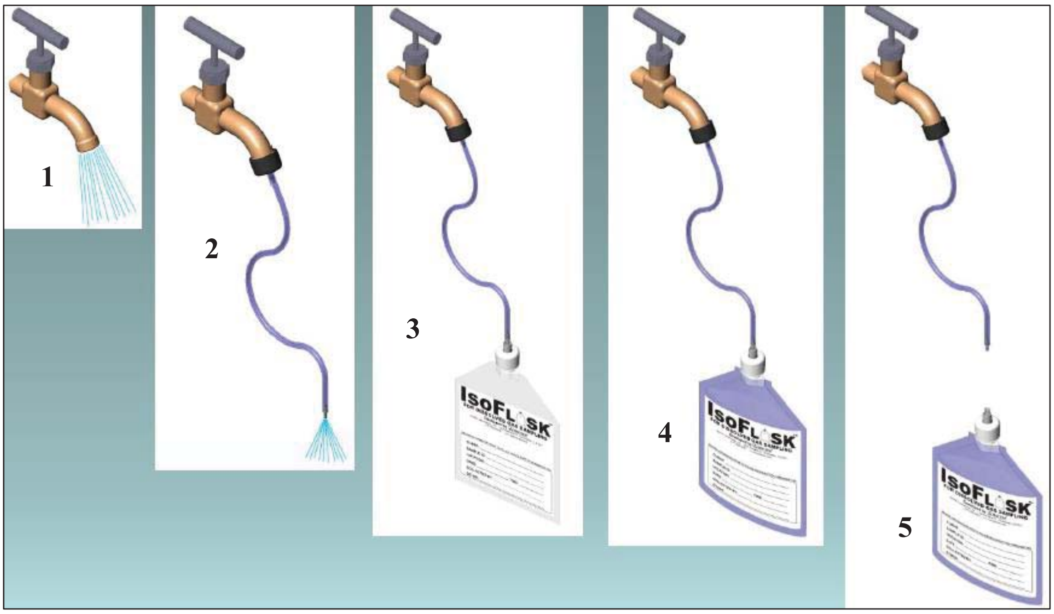
IsoFlask®

IsoFlask**®** is a flexible, evacuated plastic container preloaded with a bactericide capsule. It has a valve that enables direct connection to the outlet of the low-flow purging equipment thereby collecting the sample of groundwater and any exsolving gases (Isotech 2014c). This is a closed system in which samples are completely isolated from the atmosphere during the sample collection process. The IsoFlask**®** is evacuated in advance.

Sample collection procedure

Steps that can be followed when collecting groundwater sample for DO analysis using the IsoFlask**®** are shown in Figure 14. Isotech (2014c) outlines the step as follows:

1. Set-up the low-flow sampling equipment and purge the borehole (using the guidance in section 4.4 of the *PRE-SAMPLING PHASE*) and the sampling line,
2. When sufficient purging has been achieved as indicated by stabilisation of measured field parameters, attach the fill tube and purge to bleed the fill tube,
3. While the water is still flowing attach the evacuated IsoFlask**®,**
4. Fill the IsoFlask® to volume recommended by the manufacturer, and
5. Detach the IsoFlask® from the fill tube, close it and store refrigerated.
6. A capsule filled with bactericide is also been inserted in the IsoFlask® for preservative purposes.
7. When sampling is completed, stop the pump, disconnect and clean the equipment. If contaminated, follow equipment decontaminated guideline procedures given in
8. Table **26**.



Source: (Isotech 2014c)

Figure 14 Schematic showing steps (1-5) of collecting a groundwater sample for DG analysis using the IsoFlask® container

A summary of attributes for devices used to collect samples for DG analysis in the groundwater is presented in Table 27.

Table 27 Attributes for devices used to collect samples for DG analysis in the groundwater

Attribute	Open fill	IsoFlask®	IsoBag®	Inverted bottle
Allows collecting large gas samples	NO	NO	NO	YES
Collects only gas phase	NO	NO	NO	YES
Give an accurate concentration of the amount of gas in the water	NO	YES	YES	NO
Suitable for oversaturated DG	NO	YES	YES	YES (partially)
Suitable for undersaturated DG	YES	YES	YES	YES
Fragile	NO	NO	YES	NO
Gas pressure can be measured accurately	NO	NO	YES	YES (partially)
Obtain averagely weighted sample	NO	NO	YES	NO

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CHAPTER 7 SAMPLING RECORDS AND CHAIN OF CUSTODY

7.1 Introduction

The manual has provided comprehensive description of the process on planning, collection, preparation and handling of groundwater samples up the point they are submitted to the analytical laboratory. Additional important requirement is to keep a record during each of these sampling runs. This is the first of two important field record forms, and is called the “Field Record Sheet”. The second of these forms is the “Chain of Custody” form.

These two forms, when filled in for a sampling run, comprise the written record which documents the sample identity from collection to analytical result. In sampling programs related to legal actions, proper chain of custody procedures is crucial. To be admissible as evidence, sample results must be traceable back through their collection, shipment and analysis, so that the court is satisfied as to how the sample results submitted as evidence were collected, transferred and claimed. This is accomplished by a written record which documents the sample identity from collection to introduction as evidence.

8.2 Field record book

The Field Record Sheet is where the sampler records each step that she/he takes during the sampling of a specific borehole, or water sampling point. As each and every monitoring program will have varying conditions and aims, so each field record sheet will vary. Thus, you must prepare these for the programme. There are a number of items that will appear regularly, and these are listed below. If you carry out a Google search, you will locate numerous examples. The contents of a field record sheet usually comprise the following:

General data

1. *The header will include the organization logo, addresses, and the phrase “page .... of .... pages”,*
2. *Project name,*
3. *Date of sampling run,*
4. *Any license or authorization details,*
5. *Name of person(s) sampling, and*
6. *Weather conditions on the day of sampling.*

Sampling site data

1. *Borehole name – you can have a few columns, so that on one sheet a few sets of borehole data can be recorded. You do not need a separate sheet for each borehole,*
2. *Sample ID recorded on bottle and on Chain of Custody form,*
3. *Borehole physical data: Any damage; depth to water surface, depth to bottom of borehole; calculate water level above sea level,*
4. *Sampling pump details: Type; depth of intake; pumping rate; required purging, time to purge;*
5. *Field determinants: Temp; EC; pH; Eh; DO; alkalinity; - you should have a few rows, so that readings at various elapsed times since pumping started can be recorded,*
6. *Sampler's observations on the pumped water: Colour and colour changes during pumping; odours; DNAPLs or LNAPLs,*
7. *Sample handling: Filtering; sample bottle type and size; preservatives; storage and*
8. *Provide space for additional notes at the end of the sheet.*

Many sampling programmes will require the sampling of waters from sources other than boreholes. These could include; boreholes, seeps, springs, rivers, dams, domestic water points, reticulated water systems, and more. Devise a method of including these on the Field Record Sheet.

7.3 Chain of custody

There are occasions when the results of a groundwater monitoring program will be used as evidence in a legal dispute. To be admissible as evidence, sample results must be traceable back through their collection, storage, handling, shipment and analysis so that the court is satisfied how the sample results submitted as evidence were collected, transferred and claimed. This is accomplished by a written record documenting the sample identity from collection to introduction as evidence (Karklins 1996).

The Chain of Custody form (often shortened to COC) is the document that lists all the persons that have access to the samples. Thus, the sampler hands the samples (and custody) to the designated laboratory person, who hands them (and custody) to the designated person(s) carrying out the various required analyses. There may be a few persons in between, such as the courier recipient, the courier deliverer, or a head office staff person. All of these must sign the Chain of Custody form. A sample said to be is in custody (Karklins 1996) if it is:

1. In physical possession, or
2. In view, after being in physical possession, or

3. Secured so that no one can tamper with it.

For this manual, *Field Chain of Custody Procedures* from the Wisconsin Groundwater Sampling Manual (Karklins 1996) is given in this manual as an example:

1. *Limit sample collection and handling to as few people as possible. If sample transfers to another person are necessary, use signed receipts of possession. The chain of custody record must accompany the samples. Keep a copy of the chain of custody record for your own records.*
2. *If the samples are known or suspected of being hazardous, give a receipt for each sample collected to the property or facility owner. The property or facility owner may request split samples.*
3. *If the samples are known or suspected of being hazardous (e.g., explosion or corrosion hazard), special shipping procedures may be required by the courier. Check with the courier for restrictions and procedures.*
4. *Record field measurements and other important data on Field Record Sheet that meets site specific needs. For legal purposes, indelible ink should be used for recording all data. Errors in field records should be crossed out with one line and initialled.*
5. *When required or applicable, use photographs to document sample locations, pollution sources, violations, etc. Preferably, use a camera that print the date on which the photos were taken.*
6. *Make sure that samples are safely packed so they do not break during transport. If field blanks and/or trip blanks are required, include them in the same packing case. Maintain physical possession of the collected samples until they are properly transferred to the laboratory custodian or the courier.*
7. *Obtain a sample possession transfer receipt (a copy of the dated and signed chain of custody record) after transferring possession of the samples to the laboratory custodian or the courier.*

An example of COC form can be found in Appendix 1.

A number of statistical methods to evaluations the precision of the analytical laboratories is available (Nielsen and Nielsen 2006; Nielsen 1991; Sundaram 2009). For details of these and other ways of evaluating the overall uncertainty of sampling and analysis one should see a comprehensive guide by Ramsey and Ellison (2007).

CHAPTER 8 QUALITY ASSESSMENT

The uncertainties associated with both the sampling process and laboratory analysis can contribute variability of the results. The quality of both the sampling process and laboratory analysis must therefore be evaluated.

8.1 Evaluation of measurement uncertainties

The measurement uncertainty for the result finally obtained from the laboratory constitutes of two components; groundwater sampling and laboratory analysis uncertainties. Uncertainty of measurement is the most important single parameter that describes the quality and therefore reliability of measurements (EURACHEM/CITAC 2007). The results are used to make important decisions in respect to the goals and objectives of the monitoring and these decisions are therefore affected by these uncertainties.

Traditionally, groundwater practitioners in the country (and many other regions) are more concerned about quality of measurements within the laboratory. It is from this traditional belief, that in most groundwater quality monitoring projects or jobs the use of an accredited laboratory (local or international) is a requirement and also important criteria for review of the work. In most cases, it does appear that if the water samples have been analysed by an accredited laboratory, the results are acceptable.

While the accreditation of analytical laboratory and therefore its credibility is very important to uphold quality and integrity, the same should be said about the sampling process. The quality and credibility of a sampling process is completely left to the responsibility of the appointed groundwater practitioner expert without any criteria to evaluate the quality and integrity of the sampling process. Perhaps the quality and integrity of the sampling process is evaluated based on trust or experience of the groundwater practitioner. However, without any form of scientific criteria to evaluate the quality and integrity of the sampling process, then any other person without the knowhow of a trained groundwater practitioner can simply collect a sample and submit it to the laboratory for analysis.

Unlike the laboratory analysis that still has at quality control through accreditation, sampling processes has a wider range of factors that could influence the final results. It has become increasingly apparent that sampling is often the more important contribution to uncertainty and requires equally careful management and control (EURACHEM/CITAC 2007). The quality and integrity of both the sampling process and laboratory analysis must be scientifically evaluated based on the uncertainty of measurements in line with the monitoring goals.

Most of the information presented in this section is summarised from the EURACHEM/CITAC (2007) guide for measurement of uncertainties arising from sampling. The EURACHEM/CITAC guide comprehensively describes various methods that can be used to estimate the uncertainty of measurement, particularly that arising from the processes of sampling and the physical preparation of samples. For the purposes of this guide, only a summary of the methods which can be used to scientifically evaluate the measurement uncertainties associated with the groundwater sampling and laboratory analysis is presented. For detailed calculations see EURACHEM/CITAC (2007) and Guigues et al. 2016). Estimation of the measurement uncertainty for sampling and analysis can be done using following general steps:

Step 1: Identify sources of uncertainty

This is done through reviewing of all documents, such as the sampling methods and analysis protocols. The main sources of uncertainty include:

- Sampling collection – methods, samplers and etc.,
- Decontamination of sampling equipment,
- Pre-treatment and filtration,
- Preservation and transportation
- Laboratory analysis

Step 2: The design of the specific study (done during sampling program)

A specific study within the sampling program is designed to investigate the influence of the main sources uncertainties identified in step 1. The design has to be done during development of the monitoring program and setting of DQO. Different designs exist, and users of the manual should consult EURACHEM/CITAC 2007 and Guigues et al. 2016 for specific guidance. This step also involves selection of the main determinants to use for uncertainty estimation. These should be determinants of interests with regard to monitoring goals. Best is to select at least one parameter or chemical species from each group e.g.

i. In situ physico-chemical parameters,
ii. Major constituents,
iii. Organic matter and
iv. Pollutants of interest

Step 3: Estimation of the measurement uncertainty

The overall uncertainty of measurement is calculated based the sum of sampling and analysis variance (Equation 5 and Equation 6).

$$u^2_{measurement} = u^2_{sampling} + u^2_{analytical}$$

Equation 5

Where $u^2_{measurement}$ = measurement variance, $u^2_{sampling}$ = sampling variance and $u^2_{analytical}$ = sampling variance

The expanded uncertainty (U) can be calculated with a coverage factor, k = 2 (JCGM 100, 2008) using Equation 6.

$$U = 2u$$

Equation 6

The determinant (D) is expressed as $d \pm U$ with d being the best estimate of the measured determinant D

Estimation of the measurement uncertainty

The groundwater practitioner responsible for sampling must be able to select an appropriate method to evaluate the uncertainties associated with sampling and laboratory analysis. The uncertainty must be reported in the results and its interpretation. Without the uncertainty of measurement, the results have a limited meaning and hence might be regarded as incomplete. This is particularly important for compliance monitoring.

Ion balance Error (IBE)

The overall quality of Laboratory analysis can be quickly checked by analysis of the IBE (Equation 7Equation 7).

$$IBE\ (\%) = \frac{\sum Cations(meq/L) - \sum Anions(meq/L)}{\sum Cation(meq/L) + \sum Anions(meq/L)} x100$$

Equation 7

Where: ΣCations is the sum of cations (meq/L) and ΣAnions is the sum of anions (meq/L)

An IBE of ±5% is generally considered acceptable. However, you're reminded that IBE is not a measure of good sampling procedure, because groundwater samples collected using inappropriate techniques can still produce a good IBE if they are analysed accurately by laboratory. The main causes imbalance IBE include (Environment Agency 2002; Nielsen and Nielsen 2006; CL: AIRE 2008):

- Incomplete chemical analyses,
- Errors in the analysis of individual species (e.g. poor equipment calibration),
- Errors due to the inappropriate analytical technique),
- Contamination of samples during analysis,
- Incomplete reporting of chemical analyses and
- Errors related to the groundwater sampling process (e.g. field measurements, filtration or preservation methods).

8.2 Reporting groundwater sampling results

The objective is always to ensure consistent and reporting of the analytical results and groundwater sampling procedures. When reporting the groundwater sampling analytical results, it is important to **include the followings aspects in order for the reviewer or regulator** to see that the sampling and analysis was appropriately done in line with scientifically acceptable methods (CL: AIRE (2008):

1. *Details of borehole drilling, construction and development,*
2. *Purging and sampling equipment and devices used and justification/rationale for their selection,*
3. *Purge technique (including volumes removed and stabilisation criteria),*
4. *Any visual observations made on the sample,*
5. *Field measured parameters*
6. *Filtration of the samples (including justification, procedure and devices used), whether samples were filtered or*
7. *Detailed description of preservation techniques and reasons,*
8. *Storage conditions, transport and holding times,*
9. *Details of equipment decontamination,*
10. *Results and interpretation of quality control sample,*
11. *Analytical results from the laboratory (How the data is interpreted depends on the goals of the sampling program) and,*
12. *Evaluation of the overall uncertainty of sampling and analysis.*

References – Quality assessments

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CHAPTER 9 SAMPLING FROM SPRINGS, SEEPAGE, PITS ND LARGE DIAMETERS WELLS

9.1 Springs

For sampling purposes, a spring should be treated similarly to a borehole, except for two differences. Firstly, a spring flows continuously, so there is no need to purge. The second difference is a complication. You must be very careful not to allow contamination of this inflowing water with standing water. The best way to reduce contamination is to use the borehole sampling pump and put it in the flowing water as close to the spring outlet as possible. Measure field parameters, record results, rinse sample bottles and collect samples as you would for a borehole. Electrode measurements can be made from a little pool close to the spring outflow provided that the water velocity is not too great to cause distortion of the electrode readings. Also, be aware that it is easy to damage the sensitive parts of an electrode by touching the side of a water catchment.

A useful tool is a borehole-pointing spear. This is a short section of stainless steel borehole-screen with a point at the end, and connected to a length of metal casing. The spear is pushed into the source, the sampling pump lowered down the inside, and a sample can be collected without problems of grit jamming or damaging the sampling pump. After inserting the spear, allow a period of time for turbidity caused by inserting the spear to disappear.

If the monitoring program is to continue for a long period then temporary shallow piezometer should be installed. Ensure the Monitoring Program Guide has detailed instructions and maps on how to access this borehole-point. Wetlands are eco-sensitive, and random walking will cause damage.

9.2 Groundwater seepage

If you plan to sample the seep only once, dig a small pit in the seep zone, let it flow until the water runs clear and sample as for a spring. After sampling, return the dug sods and restore the area. If necessary, install a temporary piezometer in the middle of the seep, develop it, and return the following day when the water has cleared. If you are planning to sample the seep periodically then install a semi-permanent piezometer.

A problem with seeps is that the rate of flow can be slower than the rate of volatilization of organic compounds and slower than the drift in pH, Eh and of other parameters which depend to some extent on exposure to the atmosphere. Results should be interpreted with care.

9.3 Sampling riverbed pits

Sometimes pits dug in a dry riverbed need to be sampled. These pits can be animal dug, or a source of drinking water for a rural community, or self-dug in order to get a water sample. These can be regarded as springs or seeps.

If the sampling program is to assess drinking water fitness for use, then collect two samples. Collect the initial sample using your specialized sampling equipment to assess the intrinsic quality of the groundwater, and a second sample using the same equipment, and method of use, that the community uses to collect their water.

If the sample is for another purpose, e.g. geochemical or isotopic work, then purge the pit and collect the water sample from the fresh inflow water. For this latter purpose the better method will be to use a metal borehole pointing spear and drive this into the sand close to the pit and collect the sample from this piezometer.

9.4 Large diameter dug boreholes

The preferred method is to use two pumps, a larger capacity purging pump, and a smaller capacity sampling pump. Place the larger capacity pump midway in the borehole and start purging. Observe the flow in the borehole and try to identify the inflow point. Place the sampling pump at this point (similar to spring sampling) and collect water samples. If you cannot observe an inflow point, then assume the inflow is at the bottom of the borehole and place the sampling pump close to the bottom.

If the sampling program is to assess drinking water fitness for use, then collect two samples. Collect the initial sample using your specialized sampling equipment to assess the intrinsic quality of the groundwater, and a second sample using the same equipment, and method of use, that the community uses to collect their water.

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APPENDICES

8.3 Appendix 1 Example of Chain Custody form

Project Name		Laboratory contact person	
Name and address of organisation		Laboratory contact details (telephone and email)	
Project contact person		Contract/Jon No.	
Project contact details (Telephone and email)			

Sample ID	Sample location	Sample type (e.g. water or soil)	Sample preservation	Sampling		Number of containers	Number of containers
				Date	Time		

Sample by:		Signature:		Date:	Place:	

SAMPLE RELINQUISHED BY: **SAMPLE RECIVED BY**

Name and organization	Signature	Date	Time	Sample condition	Name and organization	Signature	Date	Time	Sample condition

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