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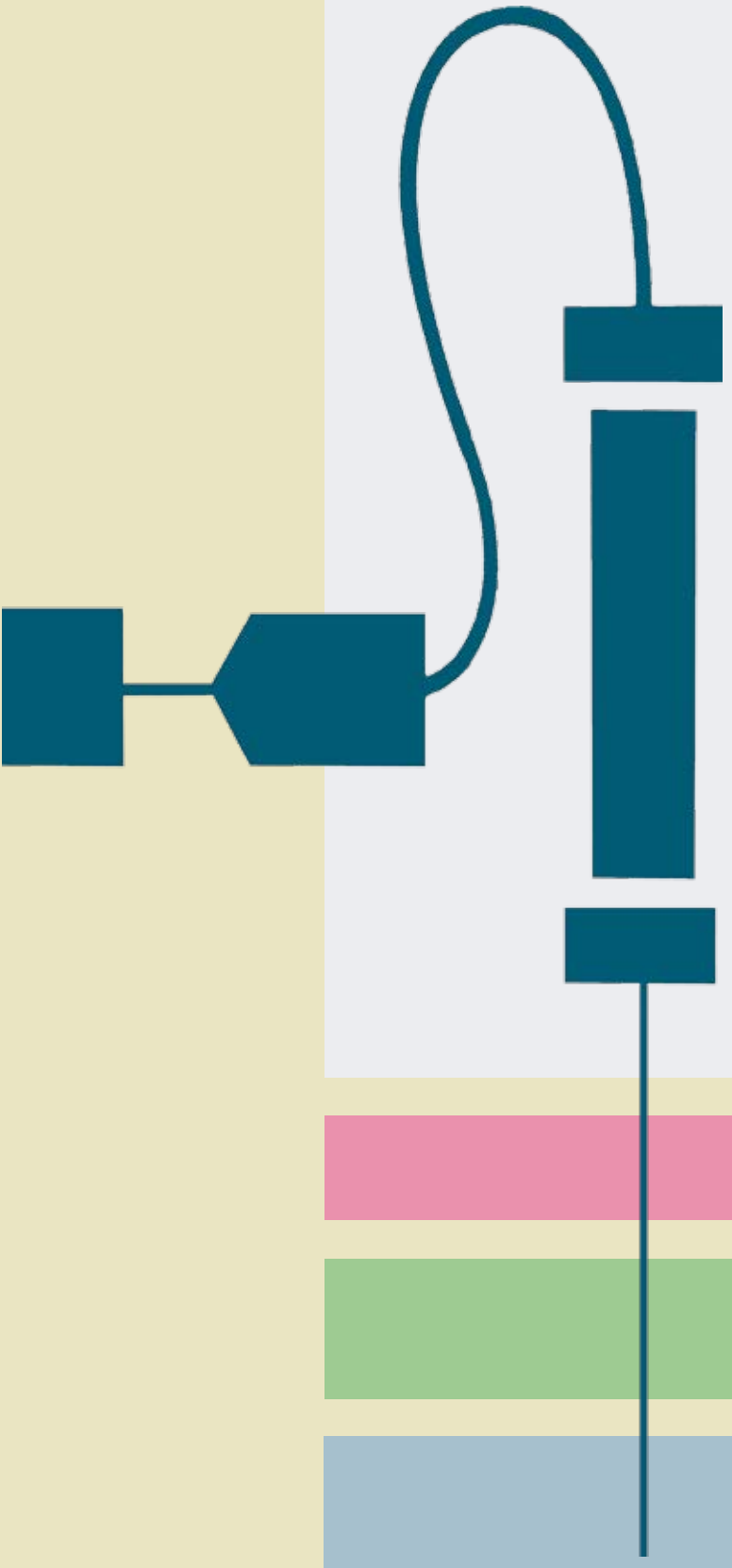

GROUNDWATER SAMPLING
(Second Edition)

TT 303/07
Water Research Commission

GROUNDWATER SAMPLING

A COMPREHENSIVE GUIDE FOR SAMPLING METHODS

Prepared for the

Water Research Commission

by

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Abbreviations and Acronyms

The use of a capital L for abbreviating litre has been adopted throughout this report.

Alk	Alkalinity
amsl	elevation above mean sea level in metres
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
Cat/An	Cations and anions
CFC	Chloro-fluoro-carbon
COC	Chain of Custody
COD	Chemical Oxygen Demand
^{o}C	Degrees Celsius (centigrade)
CSIR	Council for Science and Industrial Research, South Africa
DIC	Dissolved Inorganic Carbon
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DOC	Dissolved Organic Compounds
DOX	Dissolved Organic Halogens
DWAF	Department of Water Affairs and Forestry, South Africa
EC	Electrical Conductivity
Eh	Oxidation-reducion potential
EPA	Environmental Protection Agency (USA)
GC	Gas chromatography
HDPE	High density poly-ethylene
HPC	Heterotrophic plate count
IR	Infrared
L	litre
LDPE	Low density poly-ethylene
LNAPL	Light Non-Aqueous Phase Liquid
L/sec	Litres per second (see note above)
M	Molar (concentration) = mole/L
m^3/d	Cubic metres per day
m^3/hr	Cubic metres per hour
meq/L	milli-equivalent/litre (=mEq/L)
mg	milligrams
mg/L	milligrams per litre
µg/L	micrograms per litre
mL	millilitres
mm	millimetres
µm	micron, micrometres
µmhos/cm	micromho per centimetre (= microsiemen per centimetre)
mS/m	milli-siemen per metre, unit of electrical conductivity
MTBE	Methyl-tertiary-butyl ether
mV	millivolts

NO_x	Nitrogen oxides (collective term)
PAH	Polycyclic Aromatic Hydrocarbon
PET	Polyethylene terephthalate
POC	Purgeable organic compounds
POX	Particulate Organic Halogens
ppb	parts per billion (=µg/kg)
PPE	Personal protective equipment
ppm	parts per million (=mg/kg)
PTFE	Polytetrafluoroethylene, commonly available as Teflon®
PVC	Polyvinyl chloride
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
SF_6	Sulfur-hexafluoride
SHE	Standard hydrogen electrode
SVOC	Semi-volatile Organic Compound
TCE	Trichloroethylene
TDS	Total dissolved solids
THM	Trihalomethane
TPC	Total Plate Count (now known as HPC: Heterotrophic plate count)
TPH	Total Petroleum Hydrocarbons
TPH-DRO	Total Petroleum Hydrocarbons-Diesel Range Organics
TPH-GRO	Total Petroleum Hydrocarbons-Gasoline Range Organics
UST	Underground Storage Tank
VOCs	Volatile organic compounds
WIG	Wax impregnated graphite (electrode)
WRC	Water Research Commission, South Africa

Equivalent Terms

petrol = gasoline in USA
jet fuel = aviation fuel
paraffin fuel = kerosene

UNIT CONVERSIONS

Alkalinity:

1 meq alkalinity = 50 mg $CaCO_3$ = 61 mg HCO_3^- = 30 mg CO_3^{2-}

Atmospheric pressure:

1 atmosphere = 760 mm Hg = 101 325 Pa = 1013 hPa = 1013 mBar

Dissolved Oxygen:

1 mg/L = 31.25 µmole/L

Electrical Conductivity (EC):

1 mS/m = 10 µS/cm = 0.01 mS/cm = 1000 µS/m

Water flow rate:

1 L/sec = 3.6 m^3/hr = 86.4 m^3/d = 951 US gallons/hour = 792 UK gallons/hour

More general conversion data can be found at the URLs:

http://www.chemie.fu-berlin.de/chemistry/general/units_en.html (last accessed on 5 November 2006)

http://www.onlineconversion.com/ (last accessed on 5 November 2006)

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The first edition of this manual was written by the first author, John Weaver, in 1992. At that time he was motivated to write this manual after joining the Groundwater Research Group at the CSIR. He realized that the lack of knowledge of groundwater sampling he had at that time was probably reflective of the whole industry, both in South Africa and probably also elsewhere. This first edition of the sampling manual (Weaver 1992) proved to be one of the most popular manuals ever produced by the Water Research Commission. The edition had a print-run treble the normal one and the stock of the printed version was finished within 5 years, after which only photo-copied versions were available.

The present manual is the Second, and substantially revised, edition. For this edition two additional authors have been co-opted in order to increase the depth of the manual which reflects changes in the industry. This revised edition incorporates a number of additional sections, such as sampling for isotopes, down-hole logging etc. Some chapters have been substantially revised to include advances in field instrumentation, such as pH meter technology and increased attention to organic compounds. Other chapters have undergone only minor changes, since what was relevant in 1992 is today still relevant.

1.2 WHAT THIS MANUAL IS AND IS NOT

The purpose of the manual remains the same as the first edition, and that is to provide consistent groundwater sampling techniques that will ensure that all groundwater quality data collected is representative of in situ groundwater quality. Using these techniques will reduce sampling error to a minimum. Groundwater quality data collected according to these described techniques can then **reliably** be used to evaluate hydrogeochemical conditions.

Groundwater sampling for many years has been directed towards evaluating water quality of aquifers for water supply purposes. Closely allied to this objective has been the curiosity of hydrogeochemists, who have wished to understand the natural processes that govern changes of groundwater chemistry over the distances and time of long groundwater flowpaths. Gradually, over the past twenty or so years, and increasingly rapidly in terms of volume of research undertaken, papers published, and funding provided, attention has been directed towards contamination of groundwater. With this attention the understanding of the complex hydrogeochemical and hydrogeological processes governing the fate and transport of these contaminants has increased and continues to increase. Closely linked to this has been a proliferation of specialised sampling equipment, complex sampling techniques, and legislation governing sampling at pollution sites.

This manual does not pretend to be exhaustive and provide all the answers to groundwater sampling for all instances. What this manual does provide, is sufficient technical detail for hydrogeologists involved in water supply projects to collect proper samples, and to conduct hydrogeochemical investigations of natural systems, and forms the fundamental base for the majority of groundwater pollution investigations. However, if a highly complex, or big issue groundwater pollution project is to be tackled then the Groundwater Sampling Project Leader will need to ensure that she/he is up to date with the latest advances. The bulk of published information used for this manual derives from the USA and in particular the US EPA and the USGS. Most, if not all, of their information can be obtained by Googling or searching their websites, namely http://www.epa.gov/ and http://www.usgs.gov/ .

This manual does not describe in any detail the behaviour of determinands in the sub-surface, or any such geochemical processes. Nor are there any descriptions of laboratory analytical methods. For this type of information the reader must refer to the many excellent text books such as Hem (1992), Domenico and Schwartz (1990), Appelo and Postma (1993), Drever (1997), APHA (1998), and Fetter (1999).

1.3 SOME WISE SAYINGS

As with all activities, there are a few "wise" sayings, proverbs which seem to help one to reduce wasted time and effort and keep the job simpler. Here are some wise sayings for groundwater sampling:

- *There is no excuse for collecting a sample which, due to its method of collection, gives doubtful data.*
- *A properly collected borehole water sample is cheaper than having to return to site to re-collect a sample poorly collected the first time.*
- *A practical on-site demonstration of proper sample-collecting techniques is better training than giving the sampler this manual to self-train.*

1.4 A BRIEF OVERVIEW OF THE CHAPTERS

Chapter 2 is a broad outline of the manual. From Table 2-1, according to the field of investigation, which is either groundwater consumption, or groundwater hydrochemistry survey, or groundwater pollution monitoring, one can determine those field determinands and laboratory determinands that need to be measured. The three remaining sections are: - Planning the sampling programme, checklist of sampling equipment required in the field, and general groundwater sampling procedure.

Chapter 3 is a description of all the various laboratory measured determinands that a hydrogeologist would consider for determining groundwater quality. For each determinand or group of determinands, there is a brief description of the determinand and its characteristics followed by a detailed description of sample container, type, sampling routine and preservation.

Chapter 4 provides a detailed description of why and how the field-measured determinands, namely, temperature, electrical conductivity, pH, Eh, dissolved oxygen and alkalinity, must be collected.

Chapter 5 covers aspects of using down-hole logging of field-measured determinands.

Chapters 6 to 8 describe the documentation and procedures that must be prepared and followed during a sampling programme.

Chapters 9 to 19 describe various devices and procedures used or followed in a groundwater monitoring programme. In order these are:- sample containers and

sample preservation; water-level measurement; sample collecting devices; developing newly drilled boreholes; purging the borehole; filtering devices; flow-through cell; multiple level sampling; protective clothing; decontamination; and, sampling of springs and seeps.

Chapter 20 is a list of websites of water quality guidelines.

In writing this manual we have tried to present the information in a logical and easily understood manner without compromising scientific integrity. The style we have adopted is to use active voice verbs and personal pronouns.

1.5 REFERENCES

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

Appelo, C.A.J. and Postma, D. 1993. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam, 536p.

Domenico, P. A. and Schwartz, F.W. 1990. Physical and Chemical Hydrogeology. John Wiley and Sons, New York, 824p.

Drever, J.I. 1997. The Geochemistry of Natural Waters. Prentice-Hall, Upper Saddle River, 436p.

Fetter, C.W. 1999. Contaminant Hydrogeology. Prentice Hall, Upper Saddle River, 500p.

Hem, J.D. 1992, Study and interpretation of the chemical characteristics of natural water (3rd ed), U.S. Geological Survey Water-Supply Paper 2254, 263p.

Weaver, J.M.C. 1992. Groundwater sampling: a comprehensive guide for sampling methods. Report TT 54/92, Water Research Commission, Pretoria.

CHAPTER 2

SETTING THE SCENE AND PRE-PLANNING

2.1 WHY SAMPLE GROUNDWATER?

Why sample for groundwater quality? The answer to this important question will assist in the design of the sampling study and the field sampling program.

Groundwater is sampled for a variety of reasons

- Probably the commonest is to assess the groundwater quality for fitness for use. This fitness for use can be for irrigation, for human consumption, for use in a factory, for livestock watering, etc.
- Hydrochemical data is also used to understand the hydrogeology of an aquifer, i.e. the recharge, the flow, the water/rock interactions and the discharge processes. The ideal is to find convergence between hydrogeochemistry and the hydraulic/flow data.
- Investigations for groundwater pollution require sampling. This is both to identify and quantify the occurrence of the pollutants in groundwater and to investigate the processes around the pollution event(s).
- Water quality monitoring is the systematic collection of samples and observations on a **regular** basis to identify changes in a water body (ANZECC 2000). The quality of water resources have tended to decline worldwide due to pollution, climate changes, over-exploitation of aquifers, etc. Regular checks are therefore required to identify future risks in time, in order for remedial measures to be taken.

Whatever the intention of sampling groundwater, it is important to do the sampling properly. A properly collected sample is a water sample that, in terms of physical and chemical properties, is as close as possible to the groundwater *in situ* in the aquifer.

2.2 WHAT IS TO BE TESTED?

The selection of determinands to be analysed depends on the purpose of the water quality survey as described above and needs careful consideration. The sampling tree (Table 2.1) is a reference table that can be used to determine what field determinands need measuring and what the laboratory needs to analyse. Establish for what purpose you need to know the water quality, then refer to Table 2.1 and design your field program accordingly.

Table 2.1 Sampling tree

Aim	Application	Field measurement[1,2]	Determinands to be measured in the laboratory
Water quality for consumption	Household consumption	EC pH	Cat/An[3] Microbiology[4] Fe, Mn and other elements if a problem is suspected e.g. encrustation/corrosion
	Livestock drinking	EC pH	SO_4 F and NO_3 if a problem is suspected
	Irrigation	EC pH	Cat/An, Fe/Mn, encrustation/corrosion
	Industrial usage	EC pH Eh (Alkalinity)	Cat/An, encrustation/corrosion, Fe/Mn
Hydrogeochemistry for groundwater 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		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 pollution investigations	Waste disposal sites	pH Eh DO	Cat/An, DOC, DOX plus toxic substances of interest
	Pesticide contamination	pH Eh DO	Identified target pesticides, nitrate and potassium
	Acid mine drainage (AMD)	pH Eh DO	Cat/An, identified heavy metals
	Industrial waste pollution	pH Eh DO	Determined by the process
	Sewage disposal	pH Eh DO	Cat/An, DOC microbiology
	Underground storage tanks (UST)		DOC, Identified substances, e.g. petroleum compounds, plus degradation products
	General suspected pollution	pH DO	Cat/An, DOC, DOX.
Groundwater pollution monitoring		As required	As required

- 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.
- Temperature is usually available from the pH meter and needs to be recorded.
- Cat/An - Full analysis of major cations and anions.
- Microbiology - Includes the standard determinands for drinking-water quality.

2.3 PLANNING THE SAMPLING PROGRAMME

Possibly the most important step is to liaise with the analytical laboratory and have confidence in what they do. Establish the standard of work produced by the laboratory by requesting their accreditation credentials for the specific methods. Talk with other users of the same laboratory to find out how they experience the service. Check what output the laboratory will provide, within what time frame and cost. If the laboratory does not appear to be of a sufficiently high standard for the particular project, switch to another laboratory.

Discuss the aims of the project with the laboratory - their input can be invaluable since they may have worked on similar problems already. Time spent with the laboratory personnel can save many hours of unnecessary work. Establish what determinands need to be analysed. Discuss the laboratory's requirements in terms of sample quantities, preservation techniques and time and day to submit sample for analysis. Chapter 9 discusses Sample Bottles and Appendix C.1 lists the determinands and typical volumes required, container type, preservation and maximum holding times.

Arrange access to springs, wells, boreholes and other sampling points. This may involve having duplicate keys made or ensuring that a staff member accompanies you on the site. Notify property owners of your intentions to sample and discuss possible security issues with them. Consider the impact of sampling upon the environment, disposal of pumped water and plan rehabilitation measures. Establish from the client and/or the property owner what the liabilities would be, should any damage to property or the environment occur as a result of sampling.

Where feasible consider doing a pilot sampling run. This is a reconnaissance exercise to establish the project sampling procedure and it should be flexible but well documented. It is on this run that relevant data on each borehole is recorded. This data ranges from information about access to a particular sampling point, pump type, diameter of the borehole, purging rates, turbidity of the water and anything of relevance which will facilitate efficient future sampling of the borehole. Sampling procedures for the project as a whole are established from this pilot run. More than one run may be necessary to test various methods.

Liaise with the laboratory again to finalise such things as sample delivery and what the latest day of the week is for receipt and analysis of samples for sensitive determinands. Ensure that samples from the pilot sampling run were adequate and correctly preserved. Generally, iron out any potential problems before proceeding to the next step which is writing the Monitoring Programme Guide.

2.4 COMPILE THE MONITORING PROGRAMME GUIDE

The monitoring programme guide is a detailed document covering every possible aspect of the project (see Chapter 7). Hydrological aspects of the aquifer should be considered when compiling this guide. Sampling sequence must be worked out in a logical order visiting the least contaminated holes first to prevent cross contamination. The guide should list all boreholes to be sampled. For each borehole there must be details on its location, dimensions, purging requirements, determinands to be analysed, specific preservation and transportation procedures to be followed, indeed all relevant data. Note which sites are potentially hazardous and record any special precautions that need to be taken. If the borehole diameter is unusual and special equipment required this must be highlighted in the programme monitoring guide. Borehole/home owners should be informed of the proposed frequency of sampling runs and a mutually satisfying arrangement reached.

Having compiled the Monitoring Programme Guide regular sampling runs may commence.

2.5 CHECKLIST OF FIELD SAMPLING EQUIPMENT

The following items may be of use for field sampling of groundwater. Use this list to make your own list that is specific for the project. Add the equipment lists for specific field measurements as described in the various sections of chapter 4. The complete list will be part of your Monitoring Programme Guide (See Chapter 7). Pack equipment in the vehicle taking into consideration the order in which it will be required.

1. Borehole location

1.1. A copy of the Monitoring Programme Guide
1.2. Map or instructions for locating the sampling site or sites
1.3. Letter of introduction and visiting cards
1.4. Key to get into site and Q20™ or oil to lubricate padlocks
1.5. GPS

2. Borehole operation

2.1. Water level recorder, distilled water to clean recorder, spare batteries
2.2. Tape measure (as long as possible)
2.3. Pump or purging device, power, compressor
2.4. Downhole logging equipment
2.5. Clear plastic bailer, if you expect NAPL
2.6. Containers for purged water
2.7. Container to measure pumping rate, 25 litre or 10 litre
2.8. Sample record sheets to identify sample and/or sample sets and to record field measurements
2.9. Shovel.

3. Toolbox

3.1. Torch
3.2. Indelible ink fiber tip pen/s, pencils, ballpoint, field note book, micro-cassette recorder (especially useful for recording field notes in the rain)
3.3. Protective clothing (see Chapter 17). This includes rain gear, cold weather gear, warm clothing, sun glasses and sun hat.
3.4. Camera, plus film or memory chip
3.5. First aid kit (commercially available kits)
3.6. Drop sheet (some type of sheeting to protect instruments from contamination in the event of their falling to the ground)
3.7. Folding table or other work surface
3.8. Calculator
3.9. Personal equipment: money, driver's license, identity card, credit card, food and drink etc.
3.10 Decontamination kit, sprays, detergent, buckets, soap, rinse water and PVC pipe.

4. Field measurements

4.1. Flow-through cell
4.2. Thermometer
4.3. Conductivity meter
4.4. pH meter, electrode and buffer solutions, thermometer
4.5. Eh meter, electrode and buffer solution, thermometer
4.6. Spare batteries for the all meters
4.7. DO meter plus reagents
4.8. Wash bottle (distilled water)
4.9. Extra distilled water
4.10 Titration kit for alkalinity/acidity

5. Sample collection

5.1. Alcohol, cotton wool and matches for flaming sampling taps for micro sampling
5.2. Labels and transparent tape to cover them
5.3. Chain of Custody sheets
5.4. Sample bottles and caps plus foil and teflon inserts when necessary. Refer to Chapter 9 for bottle size and type.
  5.4.1. Always take more bottles than necessary
  5.4.2. Ensure bottles are cleaned and/or sterilised by the laboratory as needed
  5.4.3. For inorganic chemical analysis
  5.4.4. For organic chemical analysis
  5.4.5. For microbiological/virological analysis
  5.4.6. For isotope analysis
5.5. Bottles or ampoules containing preservatives (clearly labelled)
5.6. Material to spike samples for quality control
5.7. Trip blanks for VOC samples

5.8. Filter apparatus for field filtered samples, including extra filters
5.9. 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
5.10. Paper towels, rags, plus plastic garbage bags for discards

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

2.6 GENERAL GROUNDWATER SAMPLING PROCEDURE

1. Borehole setup

1.1. Find the sampling site.
1.2. Consult the Monitoring Programme Guide for specific details of the sampling site, and ensure you are at the correct sampling site.
1.3. Fill in sampling sheet i.e. weather conditions, date, time and sample number or set number.
1.4. Put down drop sheet to avoid any contamination of equipment, should it fall on the ground.
1.5. Put on protective clothing as required by the site classification.
1.6. Assemble sample kit at the wellpoint or borehole.
1.7. Remove any seal on the monitoring point, such as a locking cap or manhole cover.

2. Pre-purging activities

2.1. Measure static pre-pumped water level, record the level and rinse the water level gauge.
2.2. Perform downhole logging.
2.3. Collect free phase hydrocarbon sample
2.4. Measure the borehole depth only after downhole logging is complete.

3. Purging

3.1. Install the pump in the borehole following the specifications of the Monitoring Programme Guide (Chapter 7) for pump type and installation depth.
3.2. Install the flow-through cell
3.3. Purge the hole. Refer to the Monitoring Programme Guide for purging rates and times. If the water in the hole is hazardous, collect the purged water in a suitable container and dispose properly according to site protocol.
3.4. Measure and record the following field parameters, whilst purging the hole of stagnant water.

- temperature
- EC
- pH
- DO

3.5. Check the pumping rate. Record the rate of flow (the time taken to fill a container of a known volume) and record the quantity of water removed during purging.
3.6. Whilst purging the borehole complete sampling record sheets, log custody and label the sample bottles

4. Field measurements

4.1. When three borehole volumes have been removed from the borehole or the field parameters are stable, note the 'final' values of the field measurements
4.2. Titrate sample alkalinity

5. Sample collection

5.1. Collect unfiltered samples (see individual section on types of equipment used, methods etc). Label sample sets as you go along.
5.2. Collect samples for organic compounds - unfiltered.
5.3. Collect samples for pesticides - unfiltered.
5.4. Collect samples for sensitive non-filtered inorganic compounds (cyanide, ammonia) - unfiltered.
5.5. Collect sample for microbiology - unfiltered.
5.6. Collect sample of major cations and anions - unfiltered.
5.7. Attach in-line filter or hand filter the next sample sets.
5.8. Collect sample for dissolved trace metals - filtered.
5.9. Collect sample for phosphate, iron and manganese - filtered.

6. Wrap-up

6.1. Switch off the pump.
6.2. Protect all samples from the sun during sampling
6.3. Ensure all the necessary forms are completed.
6.4. Ensure all preservation procedures are complete.
6.5. Clean all equipment thoroughly before putting it away, rinsing with distilled water where indicated.
6.6. Clean up the site

Return the samples to the laboratory in time for analysis to be started before samples deteriorate. When in a remote area, prepare the samples for shipment to the various analytical laboratories, ensuring refrigerated transport where necessary. If the samples are to be transported by air determine whether depressurization will occur and affect the samples e.g. stoppers coming off, gases lost, evaporation of chloroform for pesticide extraction. Such samples must travel in a pressurised hold.

NOTE: Try to keep equipment as clean as possible. Wash with distilled water after use to prevent contamination. Sampling is susceptible to error and maintaining cleanliness keeps errors and contamination to a minimum.

2.7 EQUIPMENT MAINTENANCE AND REPAIR

It is much easier to repair your equipment in the office than in the field. Refer to previous field-trip notes and make sure that the necessary repairs have been done and broken equipment has been replaced.

- Check the batteries of all the meters. Do you have a spare set packed with the meter? It is not much use having the spare set in the cupboard of your office!
- For the various field meters, in the carrying-case, do you have a set of precise step-by-step instructions and are the instructions water-protected?
- The carrying cases for the various meters should be water-proof, but make sure that when you return from the field that the cases are left with the lid open so they can properly dry out. If you leave the water-proof cases shut tight any dampness will condense, both on and inside the meter, and you will end up with corroded electronics, and a faulty meter.
- Are your buffer solutions still usable and do you have enough? Have you tested your electrodes?
- Do you have a completely equipped toolbox so that you can carry out any necessary repairs in the field?

2.8 REFERENCES

ANZECC 2000. Australian Guidelines for Water Quality Monitoring and Reporting, National water quality management strategy No 7a, published by the Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand. URL: http://www.deh.gov.au/water/quality/nwqms/monitoring.html (last accessed on 17 October 2006)

CHAPTER 3

DETERMINAND SELECTION AND SAMPLING

3.1 INTRODUCTION

Modern chemistry allow for a wide range of determinands that can be analysed in water: sometimes at considerable cost. The selection of a set of suitable determinands depends on the purpose of the project. Groundwater hydrochemical studies can be divided into three broad categories:

1. Water quality surveys for the purpose of water consumption
2. Hydrochemistry surveys
3. Groundwater pollution investigations
4. Water quality monitoring

Under each of these categories there are specific subdivisions, each of which requires a different set of determinands. These are summarized in the sampling tree (Table 2.1) which can serve as a guideline for determinand selection.

The selection of determinands is very important for the effective planning of sampling and analytical protocols. You must know what to do with the results before going into the field. For exploratory efforts, i.e. when you are not quite sure beforehand what the specific requirements will be, it is better to obtain more chemical data than the immediate needs require. A minimum in such a case would be field measurements, a full major cation and anion analysis, plus a DOC analysis. Once the specific requirements are known, later sampling runs can be more selective. Bear in mind the cost implications since analysis costs can escalate rapidly with multiple samplings.

Useful determinands can be divided into five groups namely:

Field determinands (Chapter 4)

- Temperature
- Electrical conductivity (EC)
- pH
- Oxygen reduction potential (Eh)
- Dissolved oxygen (DO)
- Alkalinity.

Inorganic determinands (Section 3.2)

- Major cations and anions
- Minor cations and anions
- Trace and heavy metals
- Parameters controlling encrustation/corrosion

Environmental isotopes (Section 3.3)

- Oxygen-18 and deuterium
- Nitrogen-15
- Radiocarbon
- Tritium
- CFC and SF_6.
- Radioactivity

Organic compounds (Section 3.4) can be subdivided into specific and general groups

Specific groups

- Phenols
- Pesticides
- Petroleum derived compounds

General groups

- Dissolved organic carbon (DOC)
- Dissolved organic halogens (DOX)
- Volatile organic compounds (VOC)
- Semi-volatile organic compounds (SVOC)
- Light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL)

Microbiological indicators (Section 3.5)

- Heterotrophic Plate Count
- Faecal coliforms
- Bacteriophages
- Enteric viruses and parasites

3.2 INORGANIC DETERMINANDS

3.2.1 CATIONS AND ANIONS

The ions termed “major cations and anions” are:

K	-	potassium
Na	-	sodium
Ca	-	calcium
Mg	-	magnesium
SO_4	-	sulphate
Cl	-	chloride
Alk	-	alkalinity (carbonate plus bicarbonate)

Other species which are often included in the list for analysis and termed “minor cations and anions” are:

NH_4	-	ammonium
NO_x	-	nitrate (plus nitrite)
PO_4	-	phosphate
F	-	fluoride
Fe	-	iron
Mn	-	manganese
SiO_2	-	silica

3.2.1.1 Major ions

The major ions are the main sources of salinity in groundwater and determine the general character of the water. Excessive ions can be detrimental to its use for many purposes.

Sampling for major ions

Glass or plastic sample bottles can be used, but plastic is preferable as glass can break more easily. The rapid international growth of the bottled water industry has made PET bottles easily obtainable from the manufacturers at relatively low cost. Make sure the sample bottle is clean. For new bottles, rinse at least three times with water from the sample site (remember to include the cap) before collecting the water sample. If re-using a sample bottle, rinse with acid (e.g. dilute hydrochloric acid solution) and soak for a few days beforehand in deionised water.

Confirm with the laboratory how much sample is needed for the cation/anion analysis, as, depending on the laboratory method (especially for nitrate), up to one litre may be required.

On-site filtration is not needed for well-purged borehole water. Alkalinity needs to be measured on site if this is a critical determinand for the hydrochemical survey. However for most purposes alkalinity is sufficiently stable that it can be measured in the laboratory. Note that if phosphate is a critical determinand a filtered sample must be collected. Keep the samples cool, not specifically at 4^{o} C, but do not leave in the sun.

3.2.1.2 Ammonium and nitrate

The two nitrogen species are usually the products of pollution and most monitoring is directed to establish pollution levels.

Sampling for ammonium and nitrate

Ammonium in a water sample, if not chemically preserved, will slowly be degraded by microbiological activity to nitrate. The rate of conversion is variable. For most purposes the rate of conversion is sufficiently slow that no special preservation is needed as long as the sample is analysed within a reasonably short space of time. If the ratio of ammonium to nitrate is important, or nitrogen isotopes are to be measured, the bacterial activity must be inhibited by acidifying the water sample with

analytical grade concentrated H_2SO_4 to pH<2. Ensure that the sample bottle is correctly marked.

3.2.1.3 Phosphate

Phosphate, like nitrogen, is a nutrient, and is a critical parameter when determining eutrophication of open (surface) water. Phosphate in the form of sodium phosphate is used to increase the cleaning power of household detergents. The main source of phosphate is therefore from treated waste water. Usually phosphate is not detected in groundwater as it readily adsorbs onto soil particles. However under special circumstances phosphate may occur in the dissolved phase in groundwater.

Sampling for phosphate

Phosphate readily precipitates out onto suspended sediment or onto the sides of the sample container. Thus if phosphate is an important required determinand for the investigation, an on-site filtered sample must be collected.

3.2.1.4 Fluoride

Fluoride has severe health impacts for drinking water applications for humans and animals. It is therefore usually required for analysis for supply purposes.

Sampling for fluoride

Fluoride samples need no filtration or special preservation.

3.2.1.5 Iron and manganese

Iron levels in water above 0.5 mg/L, and manganese above 0.05 mg/L, may cause stains, especially to clothing that has been washed. A high iron concentration also imparts a metallic taste to water.

Soluble iron in groundwater is in the Fe^{2+} state (ferrous). When this water comes into contact with air, the iron is oxidised to Fe^{3+} state (ferric), which is insoluble and precipitates as ferric hydroxide (e.g. ferrihydrite), which forms a slimy, dark-brown semi-suspended material. This process often takes place in the standing water in the borehole. Manganese in groundwater behaves similarly to iron and thus the sampling procedure is the same. Mn^{2+} oxidises to Mn^{4+}.

Sampling for iron and manganese

In order to collect a representative water sample, the borehole must be properly purged and the water sample filtered, to prevent previously precipitated ferric hydroxide from ending up in the sample bottle.

The sample container can be glass or plastic. To prevent solution of previously precipitated Fe or Mn, use either new bottles or acid-washed bottles prepared in advance. Filter (0.45 micron) the sample immediately it is discharged. No preservative is needed, but keep the samples cool.

In those cases where it may be relevant to know how much precipitated iron (or manganese) is present in the form of suspended colloids in the groundwater, an unfiltered sample needs to collected and the result reported as “total iron”. The Fe level of the filtered sample is reported as “dissolved iron”. The difference between the two measurements gives the concentration of “colloidal iron”.

It is also possible to measure the different redox states of iron separately, i.e. Fe(II) and Fe(III). This is important for investigations where iron clogging is a problem or in groundwater affected by acid mine drainage. In such cases Eh and pH data are also required for proper understanding. Because Fe(II) is oxidised to Fe(III) in the presence of oxygen, it is necessary to conduct the analyses as soon as possible after collecting the sample, or even preferably to analyse the iron species in the field, if a field colorimeter is available. Test kits are available for Fe(II) and total iron determinations at various concentration ranges and levels of accuracy from suppliers such as Hach or Merck. The analysis is based on a colorimetric technique, using reagents that form a coloured complex with Fe^{2+} (Stookey, 1970, APHA, 1998). Two samples are used: one analysed directly for “ferrous iron”, Fe^{2+}, and the other digested and treated with a reducing agent, then analysed for “total iron”. “Ferric iron”, Fe^{3+}, is calculated by subtracting the ferrous iron concentration from the total iron concentration. A method for direct determination of Fe^{3+} using a selective complexing agent, acetohydroxamic acid, has also been developed, which gives more accurate speciation results (Bangthanh et al., 1999). Using filtered and unfiltered samples, the colloidal and dissolved fraction of each redox species of iron can also be determined.

3.2.1.6 Silica

Silica is sometimes required for determining the source rock of the aquifer, for water quality analysis for boiler feed-water and for some geochemical modelling. The form that silica takes in groundwater samples can be quite complex and is not that well understood. pH is a controlling factor.

Sampling for silica

Silica can appear as large colloidal particles in which case even a 2 micron filter will remove some of these particles. A 0.2 micron filter will have an even greater removal effect. Thus determine what the needs of the project are and what filtering is required before sampling. Analyses can be done on the same samples as taken for the major ions.

3.2.2 TRACE AND HEAVY METALS

Which of the many trace and heavy metals should one analyse? This depends on what information is required from the groundwater monitoring or investigation programme.

These metal ions are generally relatively immobile under normal groundwater flow conditions. Low pH and/or Eh cause the solubility of metals to increase. When low pH and/or Eh develop, as is typical at a pollution site, trace metal concentrations can rapidly increase: i.e. the metals from the insoluble phase are mobilised. Then again, when the groundwater is brought to surface, CO_2 degassing and aeration occurs causing pH to rise and the Eh to tends towards oxidising conditions causing the valence state of some of these metals to change to less soluble phases causing them to precipitate onto the sample bottle. In addition, when iron or manganese precipitate, they are strong scavengers (adsorption) that will remove many metals from the solution by co-precipitation.

From a health point of view, the important trace elements to guard against are cadmium, mercury, lead and arsenic (the dangerous four) since these have the most deleterious effects on humans.

Sampling for trace metals

It is important to filter a sample for analysis as rapidly as possible after the groundwater has been brought to surface and with minimum exposure to the atmosphere. The filtered water is acidified to pH<2 to keep the metals in solution. Some laboratories request that the sample **not** be acidified in the field. These laboratories prefer to control the acidification in the laboratory, allowing sufficient time before analysis for any metals that may have precipitated to re-dissolve.

The sample bottles can be either plastic or glass. It is best to use new bottles as old bottles may have metals adhering to the sides. The bottles must be acid-rinsed in the laboratory to ensure that all leachable material has been removed. Analytical grade nitric acid must be added to the bottle before the filtered sample of groundwater is added. The acid can be added to the bottle either in the laboratory or in the field. If the bottle is pre-acidified then acid loss can occur if the bottle is either over-filled or rinsed out. In the field acid is added either by using ampoules (recommended) or by buretting (not recommended). The ampoules contain the correct amount of acid for the sample bottle. Their narrow necks with a cut groove are easy to break without spilling. After pouring out the acid, wash out the ampoule with plenty of water before disposing of it in a rubbish bag - (do not litter). At all times when working with concentrated acid wear acid-proof gloves and protective eye-gear.

For low-level trace metal sampling it is advisable to collect a field blank as well (see section 6.2)

When a water sample is not filtered, suspended solids are collected in the sample bottle as well. If this water sample is subsequently acidified and analysed for metals the results will reflect the muddiness of the water sample, as metals will be leached by the acid from the clay particles and suspended solids. ‘Total metals’ is a determinand that is sometimes requested. This involves the acidification of an unfiltered sample. This is however a meaningless determinand for groundwater

quality as it merely reflects the muddiness of the sample. It is occasionally used during surface water quality sampling when information on contamination by transported solids, or sediments is required. So, before requesting total metals ensure you understand why you are requesting this particular analysis and how you will actually use the results.

If a laboratory receives an unfiltered water sample and is requested to analyse for selected metals, the standard practice is to let the sample stand for a few days (or centrifuge the sample) decant the clear solution, filter and analyse. This could be meaningless for groundwater interpretation purposes as, by this stage most, if not all of the metals will have either precipitated out or have been scavenged by iron and manganese.

Thus if trace and heavy metals are to be analysed for it is most important to filter the sample and to state so on the sample-bottle label. A good practice is to liaise with the analytical laboratory **before** going into the field and ensure that they know what you are doing and what you expect from them.

3.2.2.1 Hexavalent chromium

Hexavalent chromium is toxic. To analyse groundwater for Cr^{6+} is expensive and the holding-time of the sample (<24 hours) is critical. If hexavalent chromium is a possible pollutant, first analyse for total chromium and if it is present in significant amounts then arrange a special sampling run for hexavalent chromium after you have liaised fully with the analytical laboratory so that they are prepared for receiving and analysing the samples within the holding time.

3.2.2.2 Arsenic

Arsenic has been identified as an important natural contaminant of natural groundwaters, especially from sedimentary formations. Examples abound in the literature, especially from the Indian sub-continent, of its behaviour and negative health effects. Arsenic is toxic and even at low intake levels, has been directly correlated to cancer in humans. Arsenic in water occurs in two forms, namely arsenate (As^{5+}) and arsenite (As^{3+}), with arsenite being the more toxic form. Analytical methods (APHA, 1998) are available that can identify and determine the relative levels of total arsenic, arsenite and arsenate.

Sampling for arsenic

For ‘total arsenic’ no special preservation methods are required.

If the relative amounts of As^{5+} and As^{3+} are required, sampling must include in-line filtering and sample collection and storage without contact with air to prevent oxidation that may change the oxidation state. Analyse as quickly as possible after collection. There is no universal preservation method.

3.2.3 ENCRUSTATION AND CORROSION

Untreated groundwater can lead to either encrustation, or corrosion, or can have no effect on the water distribution system. In order to assess the potential of these determinands it is important to accurately measure pH in the field (chapter 4) and the cations and anions (section 3.2.1) in the laboratory.

3.2.4 EC AND TDS (TOTAL DISSOLVED SOLIDS)

"*TDS is a measure of the total mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time duration of heating.*

Residues dried at 103^{o} C to 105^{o} C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried as 180 ±2^{o} C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulphates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180^{o} C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature". (APHA, 1998)

To ask for TDS measurement by drying and weighing by a laboratory is time-consuming and expensive. EC is rapid and cheap and gives a good indication of TDS. The relationship between TDS and EC for most groundwaters is linear and

$$TDS = A \times EC$$

The factor A is between 5.5 and 9 for TDS in mg/L and EC in mS/m. A depends on the actual chemical composition of the sample. The conversion factor of 6.4 is used by the CSIR water laboratory to report “calculated TDS”. Of course, if a full analysis of the major and minor constituents is made then TDS can be calculated by summation of the ions and correcting for CO_2 loss from the carbonates.

3.2.5 Chemistry references

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

Bangthanh T.T., Nordström, D.K., Cunningham, K.M., Ball, J.W. and McCleskey, R.B. 1999. New method for the direct determination of dissolved Fe(III) concentration in acid mine waters. Env Sci & Techn 33, 807-813.

Stookey, L.L. 1970. Ferrozine: a new spectrophotometric reagent for iron. Anal Chem 42, 779 – 781.

3.3 ISOTOPES

3.3.1 OXYGEN-18 AND DEUTERIUM

Oxygen-18 analysis refers to the high precision determination of the stable isotope ratio of $^{18}O/^{16}O$ in the water molecule. Deuterium (hydrogen-2) analysis refers to the determination of the stable isotope ratio $^{2}H/^{1}H$ in the water molecule. Because of the high precision with which these ratios are measured, it has become customary to express the ratios as relative deviations from an agreed upon standard. The symbol, δ, is used to denote this deviation and is defined as:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}}{(^{18}O/^{16}O)_{standard}} \right] * 1000$$

The factor 1000 converts the ratio deviations to per mil (parts per thousands: abbreviated as ‰) which ensures that the results are expressed in manageable numbers. The identical expression is used for δD (or $\delta^{2}H$). The standard globally used for water analyses is SMOW (Standard Mean Ocean Water). This universality means that, although δ is a relative measurement, data from different laboratories are quite comparable and meaningful.

Both these pairs of isotopes are used to describe the processes to which the water has been subjected in the course of the hydrological cycle (see for example Clark & Fritz 1997, Mook 2000). In many mountainous areas there is a distinct altitude effect, meaning that lower ratios (more negative δ) are found in rainfall at higher altitudes. In some areas there is a temperature effect, derived from the fact that winter rainfall has lower isotope ratios than summer rainfall. In arid areas there is usually an amount effect, meaning that large rainfalls, or high flood events, have lower isotope ratios in the water. For most of these processes ^{18}O and deuterium variations occur in parallel, resulting in a fixed relation of 8 between the deuterium and ^{18}O isotope ratios in the water resulting in Global, or else Local, Meteoric Water Lines.

Evaporation of water from open water bodies, such as lakes, pans, rivers, and the like, results in enrichment (i.e. increase) of both isotope ratios of the water remaining in the reservoir. The rate of increase is different. A plot of δD versus $\delta^{18}O$ will show a slope of 4 to 6 and by this means evaporating water can readily be identified.

Oxygen and hydrogen isotope labels are generally very conservative underground once the water has recharged beyond a few metres depth in an aquifer. They

therefore form unique characteristic groundwater tracers for the surface water processes that occurred prior to recharge.

Sampling for ^{18}O and deuterium

Water should be collected in glass or plastic bottles with tightly fitting caps. Fill bottles close to the top. Usually 10-20 mℓ samples are sufficient.

3.3.2 NITROGEN-15

The $\delta^{15}N$ values representing deviations of the ratio of $^{15}N/^{14}N$ are reported relative to atmospheric air (AIR). The biogeochemistry of nitrogen in its path towards groundwater can be quite complex. The most commonly observed occurrence on nitrogen in groundwater is as nitrate, since ammonia is readily oxidized. In general terms three sources of nitrogen contribute to nitrate in groundwater

- Mineralisation of soil organic nitrogen
- Excess (inorganic) fertilizer transported from the soil into groundwater
- Oxidation of nitrogen from manure and septic tanks that is transported to groundwater

Each of these general categories of sources exhibits a distinct $\delta^{15}N$ range of values which can be used to identify the sources of nitrogen in water (Heaton 1986, Clark & Fritz 1997).

Sampling for ^{15}N

The samples need to be poisoned with acid, chloroform or Hg_2Cl_2 (consult the laboratory) or freezing the sample. Store cool. Sample size depends on the N-content of the water.

3.3.3 RADIOCARBON

The radiocarbon (^{14}C) content actually refers to the ratio of $^{14}C/^{12}C$ in the dissolved inorganic carbon (DIC or TIC = CO_2+HCO_3+CO_3) content of water. This ratio is quite low in natural water (10^{-12}) and is expressed in pmc (percent modern carbon). 100 pmc is the average activity of recent biological material and this is the concentration representing input into the groundwater system (see for example Clark & Fritz 1997, Mook 2000).

^{14}C is a radioactive isotope with a half-life of 5730 years. The ratio $^{14}C/^{12}C$ will therefore decrease by a factor two due to radioactive decay every 5730 years and this technique enables one to date water up to tens of thousands of years. Water in contact with carbonate soils or aquifer material will react with this carbonate and thereby reduce its ratio of $^{14}C/^{12}C$. This needs to be taken care of by assessing chemical change and the isotope ratio $^{13}C/^{12}C$ (Clark & Fritz 1997, Kalin 2000, Geyh 2001).

Atmospheric nuclear weapons tests conducted between 1954 and 1962 have released large quantities of radiocarbon into the atmosphere and this has gradually found its way through photosynthesis of atmospheric CO_2 into all living matter. In the southern hemisphere atmospheric radiocarbon values peaked to 160 pmc and thereafter reduced to 110 pmc by the year 2000. The radiocarbon content of groundwater has followed suit and elevated ^{14}C contents in groundwater are a clear indication of a contribution of recharge from the period after 1955.

Sampling for radiocarbon

If ^{14}C analysis is done by conventional (counting) analysis, then large quantities of water are required. Some extraction method needs to be used to concentrate the dissolved inorganic carbon (DIC) into bottles that can practically be transported. Field analysis of alkalinity will provide a good estimate of the DIC of the sample. Consult the analytical laboratory for equipment and procedures.

If ^{14}C analysis is done by accelerator mass spectrometry (AMS) the 0.5 to 1L water will be sufficient. No extraction will be required. Keep samples cool and in the dark. If biological activity is expected, preservation (with NaN_2 or $HgCl_2$) is required. Note that $HgCl_2$ is poisonous and should be avoided when possible.

3.3.4 TRITIUM

Tritium (or hydrogen-3) is a radioactive isotope with a half-life of 12.32 years. As such, it has the potential of being used to date groundwater 'ages' in the order of decades. The tritium levels in rainwater are extremely low and the unit used, TU, represents a $^{3}H/^{1}H$ ratio of 10^{-18}. Before the advent of nuclear weapon tests, rainfall tritium values were in the order of 3 to 5 TU. During the period of nuclear weapon tests, rainfall tritium levels reached 5000 TU in the northern hemisphere while it was never more than 100 TU in the southern hemisphere. Present day rainfall tritium

levels in the southern hemisphere are down to the pre-bomb values of 3-5 TU, while the northern hemisphere still had about 80 to 100 TU in 2000 (Clark & Fritz 1997, Gat et al., 2001).

This major worldwide contamination event has afforded the possibility of using tritium as an indicator of recent (post 1955) recharge indicator. The tritium levels in groundwater remain intact underground and are only influenced by mixing with older water and radioactive decay.

Sampling for tritium

Water should be collected in glass or plastic bottles with tightly fitting caps. Fill bottles to the top. Usually 0.5-1L samples are required.

3.3.5 CFCs and SF_6

Chlorofluorocarbons (freons) are a group of compounds that were invented during the twentieth century and that have had profound technological and environmental consequences. The levels of gaseous CFCs in the atmosphere have increased steadily at known rates since the 1950s. Since the early 1990s the growth rates have dropped off significantly (Plummer and Busenberg 2000). Three of these compounds (CFC-11, CFC-12 and CFC-113) have proved very useful as hydrological tracers. From the atmospheric levels and solubility in water it can be calculated what the different CFC levels in recent groundwater for each recharge year since 1960 would have been. Given the good chemical stability of these compounds, one therefore has an additional tool for dating and tracing of recent groundwater recharge.

Sulphur hexafluoride (SF_6) is also a man-made compound exhibiting a steady increase in the atmosphere since 1960. It is also an inert gas used in various technical applications worldwide and there are no indications that its atmospheric level will decrease. As with the CFCs, SF_6 can be used as tracer of recent groundwater recharge: the advantage is its chemical inertia and steady input function; the disadvantage is its much lower concentration in water which is due to its low solubility in water and lower atmospheric levels.

Sampling for CFCs and SF_6

Sampling for these gases requires complete isolation from the atmosphere during the transfer from underground to sample bottle. The methods require some practice to obtain reliable results that can withstand the rigours of field work and transport. Different techniques have been developed by the various analytical laboratories and close consultation with the collaborating lab is necessary to obtain the right sample vessels and sampling instructions.

3.3.6 SULPHUR-34 AND OXYGEN-18 IN SULPHATES

Sulphates in groundwater can be derived from atmospheric, pedospheric, lithospheric or industrial origin. The sources and processes by which sulphate is formed exhibit different isotope fractionations. This results in characteristic isotope ratios $^{34}S/^{32}S$ and $^{18}O/^{16}O$ in dissolved sulphate (Clark and Fritz 1997, Krouse and Mayer 2000).

Sampling for sulphate isotopes

If the sulphate content of the water is high enough and one litre of water will be sufficient for the lab, then no processing or preservation needs to be done. For low sulphate water, precipitation of $BaSO_4$ is required from an acidified sample according to the lab's instructions.

If sulphide is present in the water, its oxidation to sulphate must be prevented and it must be separated from the sulphate. A procedure with cadmium acetate has been developed to do this (Clark and Fritz 1997, p280).

3.3.7 OTHER ISOTOPES AND TRACERS

A number of lesser known isotopes and gas tracers are known to provide useful information in specific cases (Cook and Herczeg 2000).

Chloride-36 is a radioactive isotope produced in the atmosphere and by nuclear weapons, similar to ^{14}C. It has a longer half-life than ^{14}C and has been used to date groundwater up to a million years old and also to identify post 1960 recharge. The complications are that there is a production process underground and that dissolution of young chlorides may interfere with the atmospheric ^{36}Cl signal. Analysis of ^{36}Cl is by AMS.

Helium-3 is produced from the decay of tritium (^{3}H). In some cases it can therefore be used to show the initial tritium content of the water and thereby expand the use of tritium analysis to that of a true dating tool. Analysis of ^{3}He is by high-sensitivity mass spectrometry.

Helium-4 is produced by the radioactive decay of uranium, thorium and its daughters: the alpha particles produced by these materials are, in fact, ^{4}He nuclei. ^{4}He content in groundwater is therefore proportional to the time that the water has resided underground, the radioactivity of the aquifer material and some other factors (Heaton 1984). It can therefore be employed as a relative dating tool. Analysis of ^{4}He is by high-sensitivity mass spectrometry.

The concentrations of the **noble gases neon, krypton and xenon** are dependent on the atmospheric concentrations, the recharge temperature and the amount excess air that is co-absorbed by the water during recharge. Ne, Kr and Xe concentrations have therefore found applications to calculate the recharge temperature of groundwater required for palaeo-recharge studies. Analysis of these low-level noble gases is by high-sensitivity mass spectrometry.

The concentration of the **dissolved gases nitrogen and argon** in groundwater can also be used to determine the recharge temperature and excess air, provided no other nitrogen source or sink is present. Analysis is by gas chromatography.

Krypton -85 is produced when spent fuel rods from nuclear installations are processes. The ^{85}Kr content of the atmosphere has steadily increased since 1955. ^{85}Kr dissolves in groundwater at the water table and is inert underground. It therefore serves as a dating tracer similar to SF_6 and the CFCs. Analysis of ^{85}Kr is by fairly sophisticated low-level counting and requires the sampling of some 300 litres of water. The technique is therefore not often used.

Argon-39 is produced by cosmic radiation, similar to tritium and radiocarbon. Nuclear weapon testing does not produce any ^{39}Ar and, in contrast to ^{14}C, ^{3}H and ^{36}Cl, the input function of ^{39}Ar dissolved in groundwater at the water table has remained constant in recent times. Having a half-life of 269 years, ^{39}Ar should be able to date young water quite well. The difficulties of the method are that ^{39}Ar is also produced by potassium decay enhanced by the presence of uranium and thorium. Analysis requires some 10 m^3 which severely limits the application of this technique.

3.3.8 RADIOACTIVITY

The radioactivity in water is due to the presence of nuclides emitting alpha (α), beta (β) and/or gamma (γ) radiation. These are essentially contributed by the isotopes of uranium, radon, radium, potassium and to a lesser extent, thorium. When ingested, these isotopes tend to settle in parts of the body where their radiation interferes with human processes.

Gamma radiation (mainly from potassium) readily passes through the body with very little absorption and is of little health significance. Alpha particles are the main health hazards, since their range in the body is short, yet they have sufficiently high energy to cause DNA damage leading to increased cancer risk. Beta emission is considered less dangerous since the energy levels are lower.

Analyses of gross beta and gross alpha radioactivity are used as a first screening technique to identify the presence of radioactive isotopes. The actual permissible levels depend on the water use and the identification of the individual isotopes that may be present in the water (DWAF 1996).

Radon (gas) is quite soluble in water and, since it is an emanation product of uranium, is quite common in polluted and unpolluted groundwater where its level is mainly dependent on flow characteristics. It is rapidly released from surface water and can therefore serve as indicator of groundwater inflow into surface water bodies (Cecil & Green 2000).

Sampling for radioactive determinands

When planning to carry out a radioactivity monitoring programme, first consult the analytical laboratory for containers, preservation, reagents and procedures. The lab will be able to advise whether the nuclear regulator (in South Africa it is the National Nuclear Regulator) has laid down any regulations for dealing with the specific situation. The bottles are usually glass or plastic of the right properties and need to be acid-washed before sampling.

Radioactive elements are heavy metals (see section 3.2.2) and therefore filtering may be required in some cases. Radon, however, is a dissolved gas and its collection method must be one that reduces degassing and does not allow filtering.

The sample container for radon is usually supplied by the laboratory and is one that can be inserted directly into the scintillometer.

3.3.9 Isotope

Cecil, L.D. and Green, J.R. 2000. Radon-222. In: Cook, P.G. and Herczeg, A.L. eds, Environmental Tracers in Subsurface Hydrology, Kluwer, Boston.

Clark, I.D. and Fritz, P. 1997. Environmental Isotopes in Hydrogeology, Lewis Publishers, Boca Reton, NY. URL: http://www.science.uottawa.ca/~eih/ (last accessed on 17 October 2006)

Cook, P.G. and Herczeg, A.L.(eds) 2000. Environmental Tracers in Subsurface Hydrology, Kluwer, Boston, 529p.

DWAF 1996. South African Water Quality Guidelines: Volume 1, Domestic use. 2nd ed. Department of Water Affairs and Forestry, Pretoria, 190p. URL : http://www.dwaf.gov.za/Dir_WQM/docsFrame.htm (last accessed on 17 October 2006)

Gat J. R., Mook W.G. and Meijer H.A.J. 2001. Environmental Isotopes in the Hydrological Cycle, Volume 2: Atmospheric water. IHP-V, UNESCO, Paris, URL: http://www.iaea.or.at/programmes/ripc/ih/volumes/volumes.htm (last accessed on 17 October 2006)

Geyh M. 2000. Environmental Isotopes in the Hydrological Cycle, Volume 4: Groundwater. IHP-V, UNESCO, Paris, URL: http://www.iaea.or.at/programmes/ripc/ih/volumes/volumes.htm (last accessed on 17 October 2006)

Heaton, T.H.E. 1984. Sources of the nitrate in phreatic groundwater in the western Kalahari. J of Hydrol 67, 249-259.

Heaton, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chem Geol, 59, 87-102.

Kalin, R.M. 2001. Radiocarbon dating of groundwater systems. 111-144. In: Cook, P.G. and Herczeg, A.L. (ed), Environmental Tracers in Subsurface Hydrology, Kluwer, Boston.

Krouse, H.R. and Mayer, B. 2000. Sulphur and oxygen isotopes in sulphate. 195-232. In: Cook, P.G. and Herczeg, A.L. (ed), Environmental Tracers in Subsurface Hydrology, Kluwer, Boston,

Mook, W.G. 2000. Environmental Isotopes in the Hydrological Cycle, Volume 1: Introduction. IHP-V, UNESCO, Paris, 280p. URL: http://www.iaea.or.at/programmes/ripc/ih/volumes/volumes.htm (last accessed on 17 October 2006)

Plummer, L.N. and Busenberg, E. 2000. Chlorofluorocarbons, 441-478. In: Cook, P.G. and Herczeg, A.L. (ed), Environmental Tracers in Subsurface Hydrology, Kluwer, Boston.

3.4 ORGANIC COMPOUNDS

Organic compounds have primarily carbon, hydrogen and oxygen as the main components of their structural framework. In natural uncontaminated groundwater most dissolved organic compounds are fulvic and humic acids. DOC (dissolved organic carbon) analyses show the common range in uncontaminated groundwater to be from 0.1 mg/L and up to 10 mg/L.

From a water quality viewpoint, the man-made organic compounds and their impact on groundwater, is of increasing concern. Organics in groundwater is a field in which many questions are only partially answered or even remain unanswered. Extensive work is being carried out, especially in the USA and also Europe, to understand these impacts. These studies include developing analytical techniques, refining sampling methodology, understanding the subsurface behaviour of these organic compounds and understanding their effect on groundwater consumers. One reason for concern is that a number of these compounds have been identified as being carcinogenic. This latter aspect is quite an emotional matter and the reader is urged to obtain and read an editorial in “Groundwater” entitled Toxicological Risk Assessment (Lehr, 1989).

"The number of identified man-made organic compounds now totals nearly 2 million and is growing at a rate of about 250 000 new formulations annually, of which 300-500 reach commercial production. More than 1200 individual man-made organic substances have been identified in drinking water supplies This number is increasing rapidly as investigations of organic compounds in water supplies are intensified" (Freeze and Cherry, 1979).

As one can thus imagine, there is considerable overlap as far as sampling methodology is concerned between the various groups of organic compounds and to go through the full potential range will be time-consuming if not impossible. For the purpose of this manual the more commonly encountered groups of organic compounds having an impact on groundwater will be looked at individually. After that the general group in terms of sampling methodology will be described.

More commonly encountered organic compounds include:

- phenolic compounds
- pesticides
- petroleum-derived compounds

General groups (suites of compounds detected by an analytical method):

- dissolved organic carbon (DOC)
- total organic carbon (TOC)
- volatile organic compounds (VOC)
- semi-volatile organic compounds (SVOC)
- light non-aqueous phase liquids (LNAPLs)
- dense non-aqueous phase liquids (DNAPLs)

Note too, that the analytical methods for organic matter in water are classified into two general types of measurements:

(1) Those that identify and quantify individual organic compounds; and
(2) Those that identify and quantify the total amount of organic compounds which have a common characteristic. These methods are the scanning methods and are used when you suspect a problem, but have not identified that there is a specific problem.

DOC is a relatively cheap parameter to have analysed, costing between one and two times the price of sodium or chloride. DOC is becoming a standard request in groundwater investigations. COD (chemical oxygen demand), is a parameter used in investigations of heavily contaminated waters such as sewage waste water. At the low levels of organic compounds usually encountered in groundwater COD is meaninglessly inaccurate and should not be analysed or requested unless serious contamination is known to occur. Depending on the laboratory, a COD analysis is two or more times the price of a DOC analysis.

3.4.1 SAMPLE CONTAINERS FOR ORGANICS

Many of the organic compounds are toxic or pose a threat at very low concentrations. In some countries the drinking water standards for some specific organic compounds are in the 0.0001 to 0.01 mg/ℓ range (= 0.1 to 10 ppb). At such very low detection levels, bias by cross-contamination is of particular concern and special care must be taken with the sample containers and with all other aspects of sample collection and transport.

Amber or brown (to reduce UV degradation) glass bottles and not plastic bottles must be used. Depending on the compound and thus analytical method used, the required sample volume varies between 25 mL and 2 L. Some laboratories prefer wide-mouthed bottles so that a stirrer can be inserted into the bottle in order to thoroughly mix an extractant with the sample water.

Bottle caps should be Teflon lined. If Teflon lined caps cannot be obtained an alternative is to use Teflon-coated woven fibreglass sheets. These are cut into squares, placed on the mouth of the bottle and the cap is screwed on.

All sample bottles must be thoroughly cleaned prior to sample collection. The accepted cleaning procedure is to wash in hot detergent solution, rinse in warm tap water, rinse in dilute hydrochloric acid, and finally rinse in distilled water. The bottles are then put into an oven at 300^{o} C overnight. The Teflon lined caps are washed in detergent rinsed with distilled water and heated to 200^{o} C overnight. After heat treatment, the bottles are capped.

Use a strongly constructed case for transport of the glass bottles - being large and made of glass they are susceptible to breakage.

3.4.2 SAMPLING EQUIPMENT FOR ORGANICS

The sampling device used to collect a groundwater sample for organic content analysis must be chosen with great care. Many of the organic compounds are considered undesirable at low concentrations. For example, the maximum level, for chloroform in drinking water is 0.1 mg/L. Thus, any device which either introduces bias due to its construction materials or to its method of pumping, should not be used when sampling groundwater for organic content analysis.

As many, if not most, organic compounds are either semi-volatile or volatile, any device which reduces pressure is not suitable i.e. suction-lift pumps, peristaltic pumps, surface located centrifugal pumps and air-lift pumps. Gas-driven piston pumps have limited suitability for volatile organic sampling. An electric submersible is a centrifugal pump, and relies on a pressure difference behind and in front of the impellor blades to pump water. This pressure difference can introduce bias, and for very sensitive projects will be unsuitable. However for investigations where data accuracy is less stringent, electric submersibles can be used. Syringes are suitable but cannot be used to purge the borehole.

Bailers are unsuitable except in two specific cases when they are the method of choice. These two cases are when either LNAPLs or DNAPLs are present i.e. floating organic compounds or sinking organic compounds. In either case use a clear-wall bailer so that you can get an indication of the thickness of the layer of organic compounds. Other than in these two specific cases, bailers have limited suitability.

The sampling pump of choice is a bladder pump (section 11.1). Many of these are made of Teflon (PTFE). However Parker and Ranney (1997a, 1997b) (see chapter 18) investigated decontamination of sampling equipment and showed that PTFE, LDPE, and the more adsorptive polymers, tended to absorb higher levels of organic compounds than did stainless steel and PVC. Consequently to avoid cross-contamination, these plastics need a hot detergent wash plus drying in a hot oven, whereas stainless steel and PVC could be properly cleaned using only hot detergent wash.

3.4.3 MORE COMMONLY ENCOUNTERED ORGANIC CONTAMINANTS

3.4.3.1 Phenolic compounds

Phenol is a benzene ring attached to a hydroxyl group. The empirical formula for phenol is C_6H_6O. Halogens (Cl, F, Br) and other functional groups, such as nitro-

groups and amino-groups can substitute for H on the benzene ring. All substituted phenols are referred to collectively as phenols.

Many halogenated phenols are common groundwater pollutants (pentachloro-phenol, 2,4-dichlorophenol, etc.). Chlorination of water can produce chlorophenols which impart bad taste and odour to the water, which is of concern. Generally toxicity limits for phenols are higher than the aesthetic limits (DWAF 1996).

Unfiltered water samples are collected in properly cleaned 1 L glass bottles. Analytical grade sulphuric acid is added to achieve a pH<2 (Note that H_2SO_4 is very corrosive, so handle with due care). Samples are kept cool, and must be analysed within 28 days.

3.4.3.2 Pesticides

Pesticides include insecticides, herbicides, fungicides, nematicides and molluscicides. They vary widely in toxicity to humans so that for some pesticides a few grams can be lethal, whereas for others (e.g. sulphur) many kilograms need to be ingested to be lethal. Some pesticides can be absorbed through the skin, eyes or lungs and can therefore be dangerous even though they are not swallowed. Organo-phosphorous compounds can condition the body upon repeated exposure to small doses to increasing susceptibility so that later exposure may suddenly cause acute poisoning. Some pesticides have been shown to be teratogenic (causing foetal malformation) and others carcinogenic (causing cancer).

Modern pesticides degrade when exposed to one or more of the variables: water, sunlight, temperature, pH, and bacteria. The rate of degradation is called the “half-life” of the pesticide. The degradation rate is variable, depending on the combination of these factors. Preservation methods are thus dark bottles, keeping the sample cool and analysing as soon as possible. The maximum holding time is regarded as 28 days. For some pesticides acid is added to retard bacterial activity.

Know what pesticides to analyse for by conducting a usage survey. Then consult your analytical laboratory for precise sampling instructions and sample bottles.

Some pesticides are volatile, although most are semi-volatile. It is thus good practice to have no head-space in the sample bottle. Some pesticides require specific preservation methods.

If you know beforehand from a pesticide usage survey what pesticides are expected to occur in groundwater, then use the preservation methods specific for those pesticides in addition to keeping the sample cool.

3.4.3.3 Petroleum-derived compounds

Petroleum and petroleum derived products are complex mixtures mainly of hydrocarbons (compounds of only carbon and hydrogen) plus some other compounds of sulphur, nitrogen and oxygen, and a few additives. The hydrocarbons range from the very volatile C_4 up to the heavy end C_{45+}. This is well described in Total Petroleum Hydrocarbon Criteria Working Group Series (TPH-CWG, 1998). The more common petroleum products are:-

- ***Petrol**:* Automotive petrol (also called gasoline) is a mixture of C_4 to C_{12}. Additives include methyl-tertiary butyl ether (MTBE), alcohols, and lead additives. The variety and relative amounts of additives vary for different countries. There may be more than 200 compounds in a petrol product.
- ***Napthas and solvents**:* This is a term for a variety of products in the C_6 to C_{12} range that are aromatics or mixtures with paraffins. Napthas are used as diluents for paints, solvents in dry-cleaning, softening asphalt, and in extraction processes.
- ***Aviation gasoline**:* This is a mixture of paraffins, napthenes and aromatics with a high octane rating. They are all leaded.
- ***Jet fuels**:* Comprise paraffins and napthenes in C_6 to C_{17} range.
- ***Paraffin**:* Also called kerosene, is in common use as illuminant. It has the same C range as jet fuel.
- ***Diesel fuel:*** There are 5 grades of diesel fuels for uses ranging from motor-cars, through trucks to railroad engines. The lighter diesels are mainly C_{10} to C_{14} and the heavier C_{10} to C_{20}.
- ***Fuel oils**:* Are heavier than diesel fuel, and are used for heating, or are re-refined to lighter hydrocarbons.
- ***Lubricating oils**:* Have a high boiling point. They are mostly complex mixtures of hydrocarbons and additives. The hydrocarbons range from C_{20} to C_{45+}.

These products are ubiquitous in our lives, and can be spilled into the environment in a variety of ways: overturned fuel tankers, automobile and truck crashes, spillage at the fuel pump, leakage from storage tanks, discarding sump oil; the list is long. Leakage from underground storage tanks (USTs) is probably the source which has the greatest impact on groundwater. These leakages often go undetected for years and thousands of litres of fuel can be discharged. Some well written overview references on hydrodarbon site investigations are Schwerko (1994) and New Zealand Ministry of the Environment (NZ-MoE, 1999a and NZ-MoE 1999b).

Once hydrocarbons discharge into the environment, the fuels start to “weather”. Weathering is the term to describe the loss of the volatile component, leaving behind the heavier fraction. The rate of weathering varies, thus gasoline spilled onto an impermeable surface, exposed to the atmosphere, shows changes in less than a day, but if lost from a UST beneath an impermeable cover, will weather very slowly. Other weathering processes include chemical oxidation and microbial degradation.

The heavier ends of the hydrocarbons weather slower than the light ends. The best example of very slow weathering is the brittling of the tarmac seal on a road.

The analytical methods for hydrocarbon target various hydrocarbon ranges and/or specific groups:

- ***TPH analysis***: (Total petroleum hydrocarbon) typically looks at compounds in the C_6 to C_{36} range. There are many analytical techniques that measure TPH concentrations in the environment – BUT – no single method measures the entire range. Within this group there are methods directed towards lighter ends, namely TPH-GRO (TPH-gasoline range organics – a GC method), towards middle ends, namely TPH-DRO (TPH-diesel range organics– a GC method) and towards the heavier ends, namely TPH (an IR method). If you have information on the TPH source you are investigating, discuss this with the laboratory and they will then use a TPH method suited to your problem.
- ***BTEX analysis:*** (Benzene, Toluene, Ethyl benzene, and Xylenes). This method looks at the lighter end of the hydrocarbon range, but more importantly, these are the compounds that have higher water solubilities than other compounds of this group. Thus they can migrate quite some distance from the source.
- ***PAH analysis:*** (Polyaromatic hydrocarbons, also called polynuclear aromatic hydrocarbons) This method is generally used for the middle ends, diesel and kerosene. Again they are important for groundwater as they deal with soluble compounds.
- ***MTBE analysis:*** (Methyl tertiary-butyl ether) is an additive to gasoline. It is soluble in water and can be used as an indicator of gasoline contamination. Check that MTBE is actually used in the country in which you are working. It has been banned in South Africa since 2006. Some countries use other additives, check with the producers and tailor your investigation accordingly.

Sampling of boreholes for hydrocarbons is divided into two methods depending on the presence or absence of free phase hydrocarbons floating on the surface. (see also section 3.4.4.5: *LNAPLs and DNAPLs*).

(1) Lower a clear sided bailer and collect a sample at the water-table. Check for free phase. Even a haze of hydrocarbon is regarded as free phase. If no free phase is present go to (2). If a free phase is present go to (3).

(2) If no free phase is present, measure the water level, purge the borehole, collect the water sample and preserve at 4^{o} C.

(3) If a free phase is present, then the hydrocarbon must be identified. Use a bailer and collect samples from the interface until about 500 mL has been collected. Collect the floating product in a clean amber glass jar and preserve at 4^{o} C.

An interface meter (chapter 10) is a useful tool to have, if one plans to measure many monitoring wells and regularly.

3.4.4 GENERAL GROUPS OF ORGANIC COMPOUNDS

3.4.4.1 Dissolved Organic Carbon (DOC)

DOC is an indicator of the total organic matter content of groundwater. As such it is a very useful screening tool as it is a relatively cheap parameter costing between one and two times the price of a sodium or chloride determination. In a groundwater sample the total organic carbon will comprise the dissolved (DOC) and insoluble or particulate, organic carbon. The DOC in turn comprises the volatile and the non-volatile fractions.

The concentration range of DOC in most unpolluted groundwater is typically 0.1 to 10 mg/L and is composed primarily of fulvic and humic acids. Groundwater polluted from waste disposal sites can have DOC values over 1000 mg/L, most of which are fatty acids. High levels of DOC will also be obtained if an organic drilling fluid was used and the borehole was not properly developed.

If the VOC fraction of DOC is not needed, then the DOC measurement can be done on the water sample collected for major cation and anion analysis (section 3.2.1).

If the VOC content is needed then follow the procedure outlined under VOC, section 3.4.4.3.

3.4.4.2 Dissolved Organic Halogen (DOX)

"*Dissolved organic halogen (DOX) is a measurement used to estimate the total quantity of dissolved halogenated organic material in a water sample. This is similar to previous literature references to TOX. The presence of halogenated organic molecules is indicative of synthetic chemical contamination. Halogenated compounds that contribute to a DOX result include, but are not limited to, the trihalomethanes (THMs);.organic solvents such as trichloroethylene, tetrachloroethene, and other halogenated alkanes and alkenes; chlorinated and brominated pesticides and herbicides; polychlorinated biphenyls (PCBs); chlorinated aromatics such as hexachloro- benzene and 2,4-dichlorophenol; and high-molecular-weight, partially chlorinated aquatic humic substances. Compound-specific methods such as gas chromatography typically are more sensitive than DOX measurements.*

The adsorption-pyrolysis-titrimetric method for DOX measures only the total molar amount of dissolved organically bound halogen retained on the carbon adsorbent; it yields no information about the structure or nature of the organic compound to which the halogens are bound or about the individual halogens present. It is sensitive to organic chloride, bromide, and iodide, but does not detect fluorinated organic compounds.

DOX measurement is an inexpensive and useful method for screening large numbers of samples before specific (and often more complex) analyses; for extensive field surveying for pollution by certain classes of synthetic organic compounds in natural waters; for mapping the extent of organo-halide contamination in groundwater; for monitoring the breakthrough of some synthetic organic compounds in water treatment processes; and for estimating the level of formation of chlorinated organic by-products after disinfection with chlorine. When used as a screening tool, a large positive (i.e. above background measurements) DOX test result indicates the need for identifying and quantifying specific substances. In saline or brackish waters the high inorganic halogen concentrations interfere with the analysis method. The possibility of overestimating DOX concentration because of inorganic halide interference always should be considered when interpreting results" (APHA 1998).

The DOX spectrum comprises both volatile and non-volatile components. The analytical method measures DOX as a total without distinguishing one from the other. It is however possible to quantify the volatile or purgeable organic halogen (POX) and/or the non-volatile or non-purgeable organic halogen (NPOX) by a relatively simple modification to the analytical method (with an increase in cost of course). This knowledge will be of importance when groundwater pollution remedial engineering design has to be implemented. For example, if the bulk of the DOX is volatile POX then air-stripping towers might be the only remedial action needed.

Sample containers are properly cleaned 50 mL amber glass (or clear glass stored in darkness) bottles with Teflon-lined screw caps which have a hole in the centre. The hole in the centre is so that the bottle does not have to be opened with consequent loss of volatiles. The Teflon is merely pierced and the sample removed. The sample bottle must be filled taking care to reduce any loss of volatiles by carefully filling the sample bottle without turbulence. Preserve samples at pH<2 by acidifying with concentrated nitric or sulphuric acid and keep cool at 4^{o} C. Samples should be analysed within 7 days.

As volatiles are part of DOX the only suitable sampling pump is a positive displacement pump, e.g. piston or bladder pump (Chapter 11 S*ample collection devices*). A syringe is suitable but cannot be used for purging. Also the sample must NOT be filtered, as this will cause loss of the volatile fraction.

3.4.4.3 Volatile Organic Compounds (VOC)

This group is also referred to as "Purgeable Organic Compounds (POC)" as they can be purged from water in an air-stripping tower. In such a tower the water is broken up into fine droplets and allowed to fall through up-flowing air. The VOCs evaporate and are thus removed from the water.

Petroleum-derived compounds (see section 3.4.3.3) are included in this group. Please read this section before continuing. Other compounds falling into this category are solvents and degreasers. Follow the sampling methodology as

described under section 3.4.3.3. Note that for each sample point you must collect two samples (a duplicate). Consult the analytical laboratory before going into the field to confirm the methodology. If it is known beforehand what contaminants are present, specific preservatives may be recommended in addition to keeping cool at 4^{O} C.

For an accurate assessment of subsurface conditions the suitable pump is an all-metal piston pump or a positive displacement pump made from PVC. Pumps made from the more adsorptive polymers (see section 18.3) are difficult to decontaminate. A submersible pump is not suitable for accurate assessment as the negative pressure of the centrifugal pumping action will tend to reduce the concentration of VOCs. However for a rapid assessment one may use a submersible, but regard the results with due caution.

3.4.4.4 Semi-Volatile Organic Compounds (SVOC)

These organic compounds are also known as either acid-extractable organic compounds or base/neutral-extractable organic compounds. This group includes fuel oils, dye residues, wood preservatives, plasticisers, coal tar, PCBs and other priority pollutants. Pesticides (section 3.4.3.2) are included in this group.

The recommended sampling device is a positive displacement pump made of all-metal or PVC, however there is less danger of volatilization than for VOCs, so a submersible centrifugal pump can be used if a suitable pump is not available. Use 1 L or larger, properly cleaned, amber glass sample bottles with Teflon cap-liners. Do not filter the water. Keep the sample cool at 4^{O} C.

3.4.4.5 Light Non-Aqueous Phase Liquids (LNAPLs) and Dense Non-Aqueous Phase Liquids (DNAPLs)

LNAPLs are those organic compounds which do not dissolve in water and which float on groundwater; most commonly petrol-derived products and degreasers. DNAPLs are those organic compounds which do not dissolve in water and sink to lower levels, such as chloroform, liquid chlorofluorocarbons (CFC), trichloroethylene (TCE), creosote, polychlorinated biphenyls (PCB).

Note that DNAPLs can move faster than groundwater.

These two classes of organic compounds will always be pollution related. They are measured in the borehole by using a clear-sided bailer, collecting first the LNAPLs by lowering the bailer so that the water level corresponds to the middle of the bailer. Bring the bailer to the surface and measure the thickness of LNAPL film, relating this thickness to the intake area of the bailer. Decant the LNAPL sample into a properly cleaned glass bottle and seal with a Teflon-lined screw cap. Drop the bailer to the bottom of the borehole and collect the DNAPL sample, measure the thickness of the layer, relate this to the intake area of the bailer, decant the DNAPL into a properly cleaned glass bottle and seal with a Teflon-lined screw cap.

Interface meters are a relatively new development on the market. These are similar to dip-meters, in that the interface probe is lowered down the borehole with a special measurement tape. The top and bottom of the NAPL is then measured, and an accurate thickness of the immiscible layer is noted. These are quite expensive items, and are useful when regular measurement and monitoring of NAPL polluted sites are being done.

It must be noted that the thickness of the NAPL layer in the borehole is not a true reflection of the NAPL layer in the aquifer.

3.4.5 ORGANICS REFERENCES

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

DWAF. 1996. South African Water Quality Guidelines: , Volume 1 Domestic use (2nd ed), Department of Water Affairs and Forestry, Pretoria.

Freeze, R.A. and Cherry, J.A. 1979. Groundwater. Prentice-Hall, New Jersey.

Lehr, 1989 Toxicological Risk Assessment (editorial). Groundwater, 30, (1, 2 and 3). National Water-Well Association, Dublin, Ohio, USA.

Parker, L.V. and Ranney T.A. 1997a. Decontaminating materials used in groundwater sampling devices. Cold Regions Research and Engineering Laboratory, Special Report 97-24. URL: http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR97_24.pdf (last accessed 20 September 2006)

Parker, L.V. and Ranney T.A. 1997b. Decontaminating groundwater sampling devices. Cold Regions Research and Engineering Laboratory, Special Report 97-25. URL: http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR97_25.pdf (last accessed 20 September 2006)

TPH-CWG. 1998. Analysis of petroleum hydrocarbons in environmental media. W Weisman (ed), Volume 1, Total Petroleum Hydrocarbon Criteria Working Group Series, Amherst Scientific Publishers, Massachusetts. URL: http://www.aehs.com/publications/catalog/contents/Volume1.pdf (last accessed 20 September 2006)

Hydrocarbons : recommended reading with web-sites addresses

Schwerko, E.M. 1994. Sampling and Analytical methods for petroleum-contaminated soil and groundwater: An Overview. BP Oil Environmental Technology.

NZ-MoE. 1999a. Draft Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water. Oil Industry Environmental Working Group. Published by the Ministry for the Environment, PO Box 10362, Wellington, New Zealand. URL: http://www.mfe.govt.nz/publications/hazardous/sampling-protocols-oil-may99.pdf (last accessed 20 September 2006)

NZ-MoE. 1999b. Guidelines for assessing and managing petroleum hydrocarbon contaminated sites in New Zealand. Published by the Ministry for the Environment, PO Box 10362, Wellington, New Zealand. URL: http://www.mfe.govt.nz/publications/hazardous/oil-guide-jun99/user-guide-jun99.pdf (last accessed on 20 September 2006)

3.5 MICROBIOLOGICAL DETERMINANDS

3.5.1 INTRODUCTION

The subsurface environment, both in the vadose zone and the saturated zone, has a huge microbial population and a wide variety of micro-organisms. These range from health affecting species such as *Giardia lamblia* and *Salmonella typhi* (typhoid fever) to indicator bacteria such as faecal coliforms and to the large variety of species of bacteria that mineralise organic carbon. Groundwater, from virtually any source, has living micro-organisms present. Living and viable micro-organisms have been found in water at high temperatures, in highly saline environments and even in water that is 100 000's of years old. The study of these organisms is specialised and requires a well trained microbiologist, who will apply special sampling and preservation techniques in order to obtain representative samples. It is in this latter sphere of activity that extensive and on-going research is being conducted.

For the non-specialist groundwater investigator there are various groups of micro-organisms that are sampled and analysed, called indicator bacteria. These are mainly faecal indicator bacteria, and their presence or absence is used to interpret whether faecal contamination has occurred, or has not. Typically, one will use these determinands when looking at groundwater fitness for use as a drinking water resource, domestic or otherwise. They will also be used when looking at groundwater contamination, especially when sewage contamination is suspected.

Other than for health reasons, micro-organisms should also be looked at since they catalyze nearly all the important redox reactions occurring in groundwater. The main source of energy for these bacteria is organic carbon. At a typical pollution site with a high organic carbon load, the groundwater rapidly changes from aerobic through anoxic to anaerobic conditions down the groundwater flow-path. With each of these changes there is a corresponding change in the bacterial population. The identification of which bacteria are responsible for the degradation of which organic pollutants is receiving a lot of attention. If the bacteria can be identified and cultured, the commercial implications for groundwater pollution clean-up programmes are vast. Indeed, bacteriological aided clean-up methods and brews of bacteria are commercially available and applications are increasing.

What is briefly discussed above is a vast field and involves fairly specialised collection, transport and analytical techniques. As these techniques require a manual on their own and technology is rapidly developing, only the four micro-organisms most commonly used by the general hydrogeological practitioner for health purposes are discussed below. Further information can be obtained from WHO (1996, 2004).

3.5.2 GENERAL MICROBIOLOGICAL DETERMINANDS

The two main determinands are

- Heterotrophic Plate Count Test (section 3.5.2.1)
- Faecal Coliform Test including *Escherichia coli* (*E. coli)* (section 3.5.2.2).

In addition, under certain circumstances one may also need to sample and analyse for

- Bacteriophages (section 3.5.2.3)
- Enteric viruses and parasites (section 3.5.4).

3.5.2.1 Heterotrophic Plate Count test

The Heterotrophic Plate Count (HPC) test (previously known as the standard plate count or total plate count) includes all micro-organisms which produce a visible colony on a pour plate using a nutrient-rich non-selective medium after an incubation time of 48 hours at 35 to 37^{O}C. It excludes obligate anaerobes and acid-fast bacteria which represent a significant proportion of viable bacteria in water.

The test gives an indication of the general microbiological quality of water. For groundwater that is not contaminated you will expect HPC counts of between 20 and 200 per 1 millilitre. Do not be unduly alarmed if the count is in the hundreds to thousands. However, when readings of tens to hundreds of thousands are obtained, you will need to determine what is leading to these elevated counts.

The main application of the HPC method is for monitoring the efficiency of disinfection procedures in the treatment of drinking water supplies, for evaluating the quality of water in bathing areas and for establishing after-growth or secondary contamination in distribution systems. Nevertheless, as stated above, it is a useful indicator of the general microbiological quality of water, but must not on its own be used to determine whether that source of groundwater is fit for consumption. This test is not an index of pathogen presence, and thus there are no set upper limits for any health standards.

3.5.2.2 Faecal Coliform test

The Faecal Coliform Test is an indicator test of probable faecal pollution, although some bacteria detected by this method may not be of faecal origin. The bacteria that are able to ferment lactose at 44 to 45^{O} C are known as thermo tolerant coliforms. In most waters, the predominant genus is *Escherichia*, but some types of *Citrobacter*, *Klebsiella* and *Enterobacter* are also thermo tolerant. *Escherichia coli* can be differentiated from the other thermo tolerant coliforms. *E. coli* is present in very high numbers in human and animal faeces and is rarely found in the absence of faecal pollution, although there is some evidence for growth in tropical soils. Thermo tolerant coliform species other than *E. coli* can include environmental organisms (WHO. 1996, 2004).

The presence of *E. coli* indicates recent faecal contamination. It is advisable, especially if the *E. coli* count is low, to re-sample to confirm the presence of *E. coli*. If your sample has *E. coli,* then you must identify the source and process that has caused the groundwater to become contaminated and take appropriate action.

3.5.2.3 Coliphages

A bacteriophage (also known as 'phage') is a virus that infects bacteria. *E. coli* is the host bacterium for the group of bacteriophages, called 'coliphages'. The survival rate of a coliphage is higher than that of all the indicator bacteria (faecal coliforms including *E. coli*). Therefore, the presence of coliphages combined with the absence of *E. coli*, indicates that *E. coli* was present, but that it has either died-off, or the pollution source is distant. Their importance as a water pollution indicator test is that their presence indicates the potential presence of enteric viruses or other longer living pathogens. The test is relatively inexpensive, costing about R100 compared to greater than R1000 for enteric virus and parasite analyses.

3.5.3 SAMPLING GENERAL MICROBIOLOGICAL DETERMINANDS

Sample containers

Sample containers can be glass or plastic as long as they can be sterilized at 121^{o} C for 15 minutes in an autoclave or in an oven at 170^{o} C for 120 minutes. Plastic is preferred to glass since it is less prone to breakage. The seal or cap must be able to close so that contamination cannot occur after sterilization. The sampler should contact the analytical laboratory to supply the necessary sterile bottles.

Some laboratories supply glass bottles with glass stoppers. A piece of paper or length of floss is used to prevent the stopper from permanently sticking. Note that when collecting the water sample this paper/floss must **not** be left in the bottle but must be discarded.

More information on sampling bottles is given in chapter 9.

Sampling procedures

For most investigations you will be assessing the microbiological quality of groundwater straight from the aquifer. Therefore use a sample collecting device as described in Chapter 11. Purge the borehole properly. On the other hand, if the object is to determine the water quality available to the end user, then sampling must be done right at the user's tap.

For some cases you will be trying to track down the cause or source of microbiological contamination in a reticulation system. You will then sample at the well-head, and also

at various points along the reticulation network right up to the end-user(s). When you collect water from a reticulation system, the water will most likely have been chlorinated. In order to understand whether this water is safe for consumption the free chlorine must be neutralised. Free chlorine is neutralised by adding 1 mL of 30 % (m/v) sodium thiosulphate per 1 L of sample. If this is part of the sampling program ensure that you take along sample bottles with sodium thiosulphate added prior to sterilisation. Do not add sodium thiosulphate in the field, as this would be adding non-sterile material, and could introduce contamination.

When collecting from a sampling tap, or any other pipe permanently in place, the orifice must be flame-sterilised. Using tweezers to hold the cotton wool, dip some cotton wool in alcohol, set alight and play the flames around the orifice.

DO NOT FILTER THE WATER.
When collecting the water sample from any source, open the bottle and keeping the cap in one hand, hold the bottle under the discharge pipe, leave some air-space and then replace the cap. Do not rinse the bottle: just fill it up and close it. Be very careful not to touch the inside of the cap or the bottle. Record the time and date of sampling on the sample bottle. Store the filled bottles on ice (4^{o} C) and in darkness. Ideally the sample should be plated out in the laboratory within 6 hours, but within 24 hours is quite acceptable. The maximum holding time for obtaining realistic results is 48 hours.

Table 3.5.1 Sample size requirement and holding time for HPC and FC

Determinand	Sample Volume	Recommended Holding Time	Maximum Holding Time	Incubation Period
Heterotrophic Plate Count Faecal coliforms Coliphages	Total 1 L	6 to 24 hours	2 days	48 hours 24 hours 8 - 24 hours

3.5.4 ENTERIC VIRUSES AND PARASITES

Enteric viruses multiply in the gastro-intestinal tract of warm- blooded animals. They include enteroviruses, reoviruses, adenoviruses and rotaviruses as well as the hepatitis A and Norwalk viruses. Polio, echo and *Coxsackie B* are reported as "enteroviruses". These viruses can survive for some time in nature and can be transmitted via water. The viruses of major concern in health aspects are the Coxsackie A, adenoviruses, hepatitis A, rotaviruses and Norwalk viruses. The parasites of concern are *Giardia lamblia* and *Cryptosporidium parvum*.

Sampling for enteric viruses and parasites

Sampling for enteric viruses and parasites is complex. The equipment required is a large container for water pumped from the borehole, a pressure pump, and a filter cartridge with sterile glass-fibre filters. Groundwater is pumped into the container so that a known volume can be filtered. The volume filtered can vary between 100 to 1000

litres. The enteric viruses and parasites are strained onto the filter, which is then placed into a sterile bag, kept on ice and despatched to the analytical laboratory. As can be appreciated this is a fairly complex method, and the equipment is specialised. If the test needs to be done, locate a method-capable laboratory that will supply the sampling equipment, will give detailed instructions, and will train the sampler.

Table 3.5.2 Sample size requirement and holding time for enteric viruses and parasites

Determinand	Sample Volume	Recommended Holding Time	Maximum Holding Time	Incubation Period
Enteric viruses Parasites	100 L or more	Up to 24 hours	3 days	2 - 4 weeks 2 – 3 days

3.5.5 PITFALLS FOR MICROBIOLOGY SAMPLING

The microbiological population of a water sample is estimated by counting the number of colonies that develop when the water sample is cultured (grown) on a growth medium. The sample is incubated for between 12 and 48 hours after which a population count is done. Thus you must liaise with the laboratory when you plan to deliver the samples. If you can only deliver on a Thursday or a Friday the laboratory technician will have to come in over the weekend. This means that (a) you may have to pay more, and (b) if you have not made prior arrangements and the technician is away for the weekend, the sample will not be analysed and you will have to repeat the sample-run. So, if you plan to have microbiological analysis done, arrange the sampling programme to have the samples in the laboratory on Monday, Tuesday or Wednesday if feasible.

Boreholes that have been drilled by the mud-rotary method can give very high counts of micro-organisms for up to a year after installation. The drilling mud usually used is a biodegradable material such as Revert and this, being made from organic material, forms an ideal growth medium for micro-organisms. Take this into account when evaluating results.

3.5.6 MICROBIOLOGY REFERENCES

WHO 1996. Guidelines for Drinking-water Quality (2nd ed), Volume 2, Health Criteria and other supporting information. World Health Organisation, Geneva. URL: http://www.who.int/water_sanitation_health/dwq/guidelines/en/ (last accessed 22 September 2006)

WHO 2004. Guidelines for Drinking-water quality (3rd ed), Volume 1, Recommendations. World Health Organisation, Geneva. URL: http://www.who.int/water_sanitation_health/dwq/guidelines/en/ (last accessed 22 September 2006)

CHAPTER 4

FIELD DETERMINANDS

Analysis of some determinands on fresh water right at the well-head during the sampling run, are done for three reasons:

(1) to check the efficiency of purging (see Chapter 13),
(2) to obtain reliable values of those determinands that will change in the bottles during transport to the laboratory,
(3) to obtain some values that may be needed to decide on the procedure or sampling sequence immediately during the sample run.

pH and EC (and possibly DO and Eh) are measured on a continuous basis to check on the efficiency with which the standing water in the boreholes has been replaced with fresh water from the aquifer. If these determinands are stable for the duration of purging of one well volume then sample collection can start, although it is safer to wait until three purge volumes have been removed (see chapter 13)

When groundwater is removed from its natural environment to surface, several water quality determinands undergo changes due to aeration, oxidation and degassing. These determinands are:

- temperature - Chapter 4-1
- electrical conductivity (EC) Chapter 4-2
- pH - Chapter 4-3
- Eh - Chapter 4-4
- dissolved oxygen (DO)- Chapter 4-5
- alkalinity - Chapter 4-6

They must consequently be measured at the borehole preferably using a flow-through cell so that the sample is not subjected to the chemical or physical changes caused by exposing the groundwater to the atmosphere.

Temperature affects most chemical and biological reaction rates and equilibria. Temperature can be easy to measure. Phreatic water temperature is a reflection of groundwater recharge conditions and for confined water it can be a reflection of depth of flow.

Electrical conductivity is a simple indicator of all the salts in solution. Thus physical or chemical changes caused by exposure of the groundwater sample to the atmosphere can affect it. Yet it is a very helpful parameter during a reconnaissance sampling exercise.

When groundwater is brought to surface, degassing or absorption of CO_2 can occur. pH changes in the order of 2 units have been noted in some water samples. Knowledge of the in-situ pH is essential to reconstruct the potential mobility of constituents, many chemical equilibria, and encrustation and corrosion potential of the groundwater.

For monitoring groundwater pollution, the use of a flow-through cell is particularly important as in-situ polluted groundwater often has Eh below zero. Groundwater with a negative Eh, when exposed to the atmosphere, rapidly absorbs oxygen causing oxidation and precipitation of some constituents. To evaluate the mobility of pollutants in the subsurface environment, knowledge of the true in-situ Eh is essential.

Dissolved oxygen (DO) concentration is affected by aeration of the water. Thus DO needs to be measured using a flow-through cell. DO measurement is essential for groundwater pollution studies as the DO concentration (together with Eh) regulates the valence state of trace metals and constrains the bacteriological metabolism of organic compounds.

Alkalinity is measured in the field since degassing of CO_2 could cause precipitation of carbonates. If precipitation of carbonates occurs, the laboratory analytical results will reflect a lower alkalinity than is actually found in the formation water. Field alkalinity is important for carbonate rock hydrogeochemical studies and is essential for water stabilization investigations.

4.1 TEMPERATURE

Temperature is an important measurement because it affects many chemical and biological reaction rates. Temperature measurements are often the easiest of all of the in-field measurements but are still subject to error if not properly understood. The following uses for temperature measurement can be cited:

- Species solubility is temperature controlled i.e. for most species the higher the temperature the more soluble they are. The apparent exception is calcium carbonate deposition in kettles and boilers, which is actually due to CO_2 de-gassing thereby causing carbonate deposition.
- .Dissolved gas (O_2, CO_2 and N_2) solubility is temperature dependent.
- The temperature of groundwater increases with depth and temperature can therefore provide a first indication of depth of water interception. Temperature gradients in southern Africa range between 1 and 3 ^{o}C/100m.

4.1.1 EQUIPMENT FOR TEMPERATURE MEASUREMENT

A digital thermometer of the right range (typically 0-50^{o} C) and precision (0.1^{o} C) or else two mercury thermometers that can be read to 0.2^{o} C and that have been

calibrated (one is a spare as they are prone to breakage). Digital thermometers are generally accurate and are often incorporated in pH meters. Mercury in equipment is being phased out for health reasons nowadays, so it is better to invest in a good digital thermometer for field work.

Calibration of the meter should be done at least once a year (Wilde 2006). This should be done using available local facilities which are quite common nowadays when ISO and other standards are generally enforced. The chemical analytical lab is likely to have facilities being applied of follow the USGS procedure

4.1.2 FIELD PROCEDURE FOR TEMPERATURE MEASUREMENT

(1) Rinse the thermometer with flowing sample water if available, else use distilled water.
(2) Immerse the thermometer in the sample.
(3) Wait for the temperature to equilibrate. Allow sufficient time for any pipes to equilibrate if the pump has just been switched on.
(4) Read and record the temperature to the nearest 0.2^{o} C while the thermometer is immersed in the water (do not pull the thermometer out of the water to read it in the air!).
(5) Rinse the thermometer with distilled water and place it somewhere safe for future use.
(6) Do not measure the temperature in discharging water at the end of a long discharge pipe or if the flow is very low, as the water will have been heated or cooled while travelling down the pipe and will not reflect in-situ groundwater.

4.1.3 TEMPERATURE REFERENCES

Wilde, F.D. 2006. Temperature (version 6/2006): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.1. Available from the URL: http://pubs.water.usgs.gov/twri9A6/ (last accessed on 22 November 2006).

4.2 ELECTRICAL CONDUCTIVITY

Conductivity is the ability of an aqueous solution to conduct an electric current. The electric conductivity 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 conductivity 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).

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 millisiemen 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 millisiemen per centimetre or microsiemen per centimetre. All measurements must be reported in mS/m. It is not unusual to read a set of chemistry results that appear to be incorrect, only to discover that the EC has been reported as shown on the meter read-out face and thus with the incorrect units.

Conversion table for EC units

1 Siemen per cm	x	100 000	=	1 millisiemen per metre
1 Millisiemen per cm	x	100	=	1 millisiemen per metre
1 Microsiemen per cm	x	0.1	=	1 millisiemen per metre
1 Micromho per cm	x	0.1	=	1 millisiemen per metre

There are several reasons for determining the EC of a sample in the field at the time of collection rather than waiting for a laboratory measurement.

- The field determination can be used as an aid in evaluating whether a sample is representative of water in the aquifer (see Chapter 13, *Purging the Borehole*).
- An EC 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 well 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; in some cases it may be better to obtain an accurate EC determination in the field on fresh water (Wood 1981).

4.2.1 METHOD OF CONDUCTIVITY DETERMINATION

The temperature of the electrolyte affects the ionic velocities and, consequently, the specific conductance. For example, the specific conductance of potassium chloride (KCl) solutions changes about 2 percent per degree Celsius near 25^{o}C (Wood 1981).

The standard temperature for reporting EC is 25^{o}C. Thus you must measure the temperature accurately in order to correct the measured EC value to give the EC at 25^{o}C. Fortunately modern conductivity meters all have temperature sensors built into the conductivity probe compensators and thus the EC can be read directly as mS/m (or µS/cm or mS/cm) at 25^{o}C. On other meters there is a dial that has to be set to the water temperature. The direct reading meter is recommended as it saves time and, more importantly, reduces the chances of error.

With CO_2 degassing, $CaCO_3$ may precipitate from sample water and alter the cell constant in the course of time. If this happens immerse the cell in dilute HCl to clean. Other materials that may precipitate or foul the electrode are iron and organic compounds.

4.2.2 EQUIPMENT FOR CONDUCTIVITY DETERMINATION

(1) EC meter. Make sure that the EC meter you purchase can be calibrated; otherwise it is a waste of money.
(2) EC electrode, usually included with the meter.
(3) Thermometer (graduated in 0,2^{o} C), if EC meter is not temperature compensated.
(4) 1000 mL plastic beaker.
(5) Flow-through cell (optional).

4.2.3 FIELD PROCEDURE FOR CONDUCTIVITY DETERMINATION

(1) Read the manufacturer's instructions for procedures specific for your instrument and adapt these instructions accordingly.
(2) Calibrate the instrument with standard EC solution (usually KCl), either in the field or in the laboratory before leaving for the field.
(3) Start pumping the borehole.
(4) Measure the water temperature.
(5) If necessary, set the temperature dial to the observed groundwater temperature.
(6) Immerse the electrode in flowing water for a few minutes to equalize the temperature of the electrode and the water. Move up and down a few times to remove any air bubbles that may be trapped in the electrode.
(7) Take the EC reading, make sure it is in mS/m (or else converted) and record it together with the temperature.
(8) Rinse the cell with distilled water and pack away wet.

Note: Errors in reading will be made if the electrode is not fully immersed in the sample or air bubbles are present on the platinum electrodes.

4.2.4 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.

4.3 pH

pH is a measurement 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:

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

where $[H^+]$ represents the hydrogen ion (H^+) concentration in moles per litre

pH is one of the most important parameters affecting the chemical composition of groundwater. Anything that changes the pH of a sample will likely affect other constituents as well. Aeration, oxidation, mineral precipitation, temperature changes and degassing of a sample can significantly alter its pH.

The pH of pure carbon-dioxide free water at 25°C is 7.0. Above this pH, samples are considered basic or alkaline and at pH less than 7, samples are considered acidic. Temperature has a strong effect on pH measurements and must be taken into account for accurate field measurements. For example, neutral pH at 30°C is not 7.0, but 6.92 and at 0°C, it is 7.48 (Wilde et al., 2006). pH is usually reported on a scale that ranges from 0 to 14. Values above 14 and below 0 are possible in concentrated (1M) solutions, but not found in environmental waters.

For example, during a water sampling project in the Western Cape of South Africa, it was observed that CO_2 degassing from low TDS groundwater from Table Mountain Group quartzite caused the measured pH to change from 4.9 to 7.1. In practical terms highly corrosive water became mildly corrosive. If the pH had been measured in the laboratory, and not on site, pipeline design precautions might not have been taken.

pH is a parameter that controls the valence state, solubility and hence mobility of many trace metal species, which may be significant in environmental investigations. Eh-pH diagrams or geochemical models can be used to make predictions of whether a species is soluble (and hence mobile) in an aquifer. These require an accurate measurement of the pH and temperature (and Eh for multivalent species) and cannot rely on pH analysis in the laboratory a few days later (Shaver 1993). Since these parameters are unstable and will often change rapidly when groundwater is brought

to the surface, the measurements must be taken in the discharge stream as close to the borehole as possible. Although use of a flow-through cell (Chapter 15) is recommended for pH measurement, it is not essential.

4.3.1 METHOD OF pH MEASUREMENT

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.

The glass electrode is the classical method of pH measurement. pH is determined by measuring the electrical potential that develops across a glass membrane which is sensitive to hydrogen ions. ISFET is a relatively new technology using a solid state sensor that responds to the hydrogen ion (IQSI 2002). Both the glass electrode and the ISFET sensor are used in combination with a reference electrode of stable, known electrode potential connected to electric potential measuring device (high impedance voltmeter). When the electrodes are immersed in liquid, a circuit is completed through the meter and a voltage is produced that is related to the hydrogen ion activity in solution. The measured value must be calibrated to one or more aqueous pH buffer solutions of known, fixed pH.

The electrode system produces an electrical potential (E, in millivolt) that is linearly related to the pH of the water expressed by the relation:

$$E = E_0 + S*pH$$

where E_0 is a constant that depends on the electrode system and S is a temperature dependent constant that is theoretically known. To determine these two constants one therefore requires two buffers, i.e. solutions of known pH that are used to calibrate the electrode pair. Electrochemical theory predicts that:

$$S = 0.1984\ (273.15 + t)$$

where t is the temperature in degrees Celsius.

In practice it has proved to be better to check this slope, hence the introduction of the second buffer in the recommended procedure.

4.3.2 pH MEASURING EQUIPMENT AND SUPPLIES

An electrometric pH measuring system consists of:

- the pH meter (potentiometer)

- the measuring electrode
- the reference electrode (usually built into the measuring electrode)
- pH buffer solutions

4.3.2.1 pH meter

For routine work, use a pH meter accurate and reproducible to 0.1 pH unit with a range of 2 to 12 pH. The instrument should preferably be equipped with a temperature-compensation adjustment and should operate over a temperature range of 0 to 45°C. The pH meter for field measurements should be portable - a lightweight, battery-powered unit is recommended - and come in a robust casing. Waterproof models are highly recommended, particularly for work in humid areas. Many instruments have fully automated calibration routines. This can improve their ease of use, but can also restrict the choice of buffer solutions for calibration in some cases. Make sure the pH meter has millivolt reading capability if it is also to be used to measure Eh.

The pH meter should be tested before each sampling trip and properly cleaned and stored after use. Check batteries for leakage every two months. pH meters, even the field models, are sophisticated electronic equipment that require care in handling and operation. Try to keep the instrument clean and dry by using a groundsheet and portable shelter during field work. Make sure it is stored in a clean, dry place away from temperature extremes. The pH meter is usually supplied in a waterproof transport case. Do not store the pH meter in this case with the lid closed, as condensation may occur and damage the meter. Avoid unnecessary jostling or sudden impacts, which can damage fragile components or dislodge electronic connections.

4.3.2.2 Electrodes

Two electrodes are needed to measure pH:

(1) the measuring electrode (either glass electrode or ISFET sensor)
(2) the reference electrode, which provides an independent, constant potential against which to measure the unknown pH.

The glass electrode consists of a bulb of special glass containing a fixed concentration of KCl or a buffered chloride solution in contact with an internal reference electrode. When immersed in aqueous solutions, the outer layer of the glass becomes a gel layer that allows hydrogen ions to diffuse in or out, proportional to their concentration in solution. This causes a potential difference (measured in millivolts) to develop between the inner buffer solution and the external sample. The ISFET pH sensor consists of a silicon semiconductor substrate with two electrical contacts (source and drain) a small distance apart. An electrical insulator (gate) is deposited on the substrate between the source and drain. Hydrogen ions at or near the surface of the insulator cause a variable voltage potential between the insulator and the underlying semiconductor material (IQSI 2002). For both types of pH

electrodes, the potential developed is proportional to the relative concentration of hydrogen ions in the solution and is used to measure the pH. The glass electrode system is preferred over the ISFET for high accuracy applications. The advantages of ISFET sensors for environmental applications are their small dimensions, rapid response times and robustness.

The reference electrode part of the pH measuring system is usually a silver/silver chloride electrode or calomel electrode filled with electrolyte gel or solution. An electrode junction (ceramic, polymer or direct contact) allows for electrical contact between the internal electrolyte and the external solution. For general field use, a combination electrode is recommended which incorporates the measuring and the reference electrodes into a single probe available in a robust plastic envelope.

Electrode performance

Instruments that report slope as a percentage value are comparing this with the theoretical slope, S. Good working glass electrodes should give slopes better than 95% and this should remain constant. A lower slope indicates that the electrode has deteriorated and maintenance or replacement is required. Electrode manufacturers supply information on remediation procedures. Electrodes with slopes less than 90% should not be used.

Some drift in the electrode potential does occur and 0.1 to 0.2 mV per hour drift is common for a properly functioning electrode (Wilde et al., 2006).

The transistor in ISFET systems may be slightly sensitive to light and should not be used in direct sunlight.

Electrode maintenance and storage

Electrodes may give many years of reliable service if they are carefully handled, stored and maintained. Glass electrodes, especially, are fragile and should be handled delicately.

Electrodes should be rinsed with deionised water and gently blotted with soft tissue before use and in between transferring the electrode from one solution to the next. Do not touch the glass bulb with your fingers or wipe it roughly with paper towel. Oily film or scratches on the bulb may affect the pH reading and static charge caused by wiping can lead to drifting or sluggish response. Electrodes filled with gel (or solid polymer in some newer models) are easier to maintain than liquid filled electrodes.

Gel-filled electrodes do not require filling. Do not leave this in dilute solutions (e.g. deionised water) for long periods of time as salts may leach from the electrode. If the electrode becomes clogged, it may help, in some cases, to place the electrode in warm water (60°C) for a short time (one minute or less) to liquefy the salt gel and rejuvenate the junction (Wilde et al., 2006).

Liquid-filled electrodes require periodic refilling of the electrolyte solution.

- Filling solutions are usually potassium chloride (KCl) but differ in concentration for different electrodes, e.g. 1M, 3M, saturated solution. Check the manufacturer's instructions for the correct solution for your electrode.
- Remove salt crystal deposits from the outside of the electrode and membranes before use, by rinsing it with deionised water. Electrodes using saturated KCl may have some crystals inside the filling solution chamber which do not require dissolving.
- Before using the electrode, top up the filling solution so that it reaches the bottom of the fill hole on the side of the electrode.
- When measuring pH, always unplug the fill hole before use and replug afterwards.
- If the electrode has not been used for some time, it may need reconditioning by replacing the filling solution (see manufacturer's instructions). Use a syringe to drain out the old solution, flush the chamber with deionised water (several times if necessary to remove crystals) and refill with the correct solution.
- Cleaning solutions are available in the market that may extend the life of a dirty electrode.

Short term storage**:** Keep the electrode bulb of the glass electrode moist and capped when not in use and between sampling points. Drying of the bulb will lead to slow response times. Follow the manufacturer's instructions on storage solutions. A small volume of pH 7 buffer solution is usually poured into the cap before covering the bulb. Deionised water or concentrated KCl solutions should not be used to keep the glass bulb wet, unless specified by the manufacturer. Liquid-filled electrodes should preferably be stored upright when not in use (Wilde et al., 2006).

Long term storage: Drain the filling solution from liquid-filled electrodes that will not be used for several weeks or longer. Cover the bulb with a protective cap, filled with storage solution or electrolyte if recommended by the manufacturer. Rinse the outside of the electrode with deionised water and store the electrode dry (Wilde et al., 2006).

ISFET electrodes are more robust, but care should still be taken not to damage the delicate sensor tip (usually recessed into the probe). Static electricity or other electrical charges should be avoided as they may damage the transistor. For general use, rinsing the probe in deionized water then wiping dry with a soft towel or tissue will be sufficient to clean the probe. ISFET probes can also be cleaned with a toothbrush and mild detergent or soaked for not more than 3 minutes in 0.5% bleach solution (10 to 1 dilution of laundry bleach in deionised water) to remove protein build-up. An ISFET probe should be stored dry with a protective cap covering the probe tip (IQSI 2002).

4.3.2.3 pH buffers

pH buffer solutions are used to calibrate the pH meter readings. During calibration, the electrodes are immersed in a buffer solution and the instrument adjusted according to the manufacturer's instructions, so that the meter reads the correct pH value for that buffer.

Some instruments offer one-, two- or three point calibration, using up to three buffer solutions. A minimum of two buffers is recommended for routine pH measurement work. For two point calibration, buffers should be selected that bracket the expected pH range of the samples to be measured, usually with pH 7.0 buffer as one end of the bracketed range. Single point calibration can be used in the field between boreholes, to check that the instrument has not drifted between readings.

The pH of groundwater from quartzites is usually between 5 and 6, so select buffers pH 4 and pH 7 to calibrate the meter. Limestone or dolomite aquifers typically have groundwaters of pH greater than 7 and buffers of pH 7 and pH 10 should be used for calibration.

Poor quality, old or contaminated buffers will give at best inaccurate and at worst completely wrong pH readings. Advice for using pH buffer solutions (Wilde et al., 2006):

- Use certified buffers that are traceable to an internationally accepted standard e.g. NIST Standard Reference Material.
- **Note that buffer solutions obtained for measurement of pH from 4 to 10 typically have high ionic strength. For accurate work on dilute waters, obtain low ionic strength buffers.**
- Note the expiry date of the buffer solutions and copy it onto any containers into which the buffer is transferred. Discard buffers on their expiry date as the pH may have changed substantially due to carbon dioxide absorption, evaporation or mould growth.
- Always cap buffer bottles to minimise evaporation and contamination from atmospheric carbon dioxide. Buffers are stable for the short exposure time during electrode calibration. (Sensitivity of buffers to CO_2 contamination ranges from most sensitive for high pH to least sensitive for low pH, i.e. pH 10 > pH 7 > pH 4.)
- Never pour used buffer solutions back into the bottle. Always decant a small amount for use and discard after calibration.
- Never insert an electrode or other material into the buffer stock solution bottle.
- Be careful not to contaminate the buffer with another buffer or other fluids. Do not pour one buffer after another into a beaker. Always use a clean container. (pH 4 buffer is the least sensitive to contamination).
- Do not dilute buffers, for example with water dripping from the electrodes. (pH 7 buffer is the most sensitive to dilution).

- Store buffer stock solution in a fridge when not in use.
- Before using buffers, bring them to the temperature of the sample solution (e.g. by immersing sealed bottles in the sample water for five minutes).
- Check for temperature correction factors (usually printed on the side of the buffer bottle) and set the pH meter to read the temperature corrected pH value for each buffer, unless automatic temperature compensation is active. For precise determinations, the buffer temperatures should be within ±1°C of the sample solution (APHA 1998).

4.3.2.4 pH Equipment Checklist

(1) pH meter
(2) pH combination electrode
(3) pH buffer solutions of pH 4, pH 7 and pH 10 (500 mL each)
(4) 3 x 100 mL glass or plastic beakers to hold buffer solutions when calibrating the pH meter. Use plastic beakers if using a glass pH electrode in order to reduce breakage
(5) Filling solution for electrode, plus syringe
(6) Bucket to immerse buffer solution in order that the buffer solution and the groundwater are within 1°C
(7) Thermometer, if pH meter does not have automatic compensation
(8) Deionised water plus squeeze wash bottle
(9) Soft tissue to dry electrode
(10) Table or flat working surface
(11) Flow-through cell (Chapter 14), desirable, but not essential

NOTE: Low salinity or low alkalinity water is usually badly buffered: which means that the pH meter readings will not be steady. A flow-through cell will improve stability.

4.3.3 FIELD PROCEDURE FOR pH MEASUREMENT

READ THE MANUFACTURER'S INSTRUCTIONS FOR YOUR INSTRUMENT.

NOTE: There are many types of pH meters on the market, 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 your particular instrument. Some of the equipment and procedures described here may not be applicable for your instrument. If so, make sure you understand the manufacturer's instructions and adapt the procedures below accordingly.

4.3.3.1 Calibration procedure

For manual calibration, calibrate the pH meter as follows:

(1) Label beakers for pH 7 and pH 4 buffers with a waterproof marker. If alkaline water is expected, use pH 7 and pH 10 buffers.
(2) Place containers of pH 4 and pH 7 buffers in a bucket with running groundwater for 5 minutes to equalise temperature. Measure the temperature of the running water with a thermometer and set this temperature on the pH meter. (Step 2 is not needed if the instrument has automatic temperature compensation).
(3) Ensure electrode is filled with filling solution (if liquid filled) and that the junction is not clogged. Rinse the pH electrode with deionised water and blot dry with soft tissue. Gently tap or shake to dislodge any trapped air bubbles inside the electrode.
(4) From the container of pH 7 buffer, decant fresh buffer solution into the clean labelled beaker. Use enough buffer solution to cover the bulb or the FET part of the pH electrode and the reference junction.
(5) Immerse the electrode in the pH 7 buffer and agitate gently. The bulb of a glass electrode should not touch the bottom or sides of the beaker.
(6) Adjust the pH meter value to match that of the buffer pH. (Look up the adjusted pH of the buffer solution in the temperature correction tables, if there is no temperature compensation on the instrument. The tables are usually on the side of the buffer stock solution bottle).
(7) Remove the electrode, rinse with deionised water and blot dry.
(8) From the container of pH 4 buffer, decant fresh buffer solution into the next clean, labelled beaker and immerse electrode as before.
(9) Adjust the pH meter to read the second value (temperature compensated if necessary). The adjustment may either be made with the same knob, button or screw as for the first buffer, or with a separate one for “buffer 2”, “slope adjustment” or even the “temperature” knob. Check the instrument manual.
(10) Rinse the electrode, blot dry and re-check the value of the pH 7 buffer. If the value is within +0.05 pH of the original, proceed with step 11. If drift has occurred, repeat steps 5 to 9 until two successive reading are obtained without needing further adjustment. The pH meter is now calibrated.
(11) Discard all used buffer solutions.

Note: If the entire calibration procedure has to be repeated more than three times, there is probably a problem with the pH meter, electrode or buffer solutions. Abandon the calibration and measurements until the problem is found and corrected.

The third calibration buffer can be used to check the range. The pH meter should read the value (temperature adjusted if necessary) to within 0.1 pH units, otherwise the instrument should be recalibrated.

Calibrate the pH meter immediately before the first measurement of the day and then check for calibration drift with the pH 7 buffer before each subsequent reading. Check that the meter holds its slope by measuring the pH 4 or pH 10 buffer a few times during the day.

4.3.3.2 pH measurement

Always ensure the pH meter is properly calibrated (even by measuring a third buffer) before measure the pH of a groundwater sample. The pH measurement should be taken as follows:

(1) Rinse a clean beaker several times with the water to be tested and collect a fresh sub-sample from as close to the borehole outlet as possible. Do not use a bailed sample. Try to minimise aeration by using a low flow rate. Do not shake or stir the sample vigorously and do not leave it standing in the sun.
(2) Rinse the pH electrode with deionised water and gently blot dry.
(3) Insert the electrode into the beaker and stir gently while waiting for the reading to stabilise.
(4) Record the pH to the nearest 0.1 units.
(5) Rinse the electrode, blot dry and switch off.

NOTE: The tip of a glass electrode can easily be damaged due to scratching against the sides of a beaker or too vigorous drying before or after measurement. Be extremely careful with the electrode: it is expensive and breakage can ruin your field trip.

Where possible, pH measurements should be made using a flow through cell (Chapter 15), rather than using a groundwater sub-sample for measurement.

4.3.3.3 Trouble shooting pH meters and electrodes

- Do not let the glass electrode dry out. Cover it with the cap or the rubber sleeve that is supplied with the electrode and fill with a few drops of storage solution.
- Ensure the liquid-filled glass electrode is filled with KCl solution and contains no trapped air bubbles.
- Ensure that the electrode is clean. If not, clean glass electrodes by alternately immersing three times each in 0.1N NaOH and 0.1N HCl. Clean ISFET electrodes with a toothbrush and mild detergent.
- Use buffer solutions before their expiry date and decant a fresh portion for each calibration.
- For further trouble-shooting read Standard Methods (APHA 1998) or Wilde et al. (2006).
- Gel-filled electrodes should always be stored with the bulb wetted with the manufacturer's solution, never store wetted with dilute solutions.

4.3.4 pH REFERENCES

APHA 1998. Method 4 500-H+. Standard methods for the examination of water and wastewater (20th ed), Am. Public Health Assoc, Washington DC.

IQ Scientific Instruments. 2002. Frequently asked questions about ISFET "FET" pH technology. URL: http://www.phmeters.com/Islet_pH_Information.htm (last accessed 17 October 2006).

Shaver, R.B. 1993. Field vs. lab alkalinity and pH: effects on ion balance and calcite saturation index. Ground Water Monitoring Review, 13(2), 104-112.

Wilde, F.D., Busenberg, E. and Radtke, D.B. 2006. pH, U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.4, (version 1/2006). Available from the URL: http://pubs.water.usgs.gov/twri9A6/ (last accessed on 22 November 2006).

4.4 Eh (OXIDATION-REDUCTION POTENTIAL, ORP, OR REDOX POTENTIAL)

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 many metals and the degradation of organic contaminants (Appelo and Postma 1996).

Redox reactions are often very slow in relation to other aqueous reactions, which means that apart from equilibrium chemistry, reaction kinetics also play a significant role. When interpreting the measured Eh value, it cannot be assumed that the redox species coexist in equilibrium. Dissolved oxygen, for example has been found to coexist with hydrogen sulphide, methane or ferrous iron in many situations (Nordström and Wilde 2005). This means that the measured Eh may not correspond with the Eh calculated from electrochemical theory using one of the redox active elements (e.g. dissolved oxygen) in the water. Quantitative determinations of Eh using the platinum (or other noble metal) electrode method are valid only when the redox species are electro-active and are present in solution at concentrations of about 10^{-5} molal and higher (Nordström and Wilde 2005).

Eh measurement is not a routine procedure and can not be measured unambiguously in most natural waters. Eh readings are open to misinterpretation if the electrochemical theory behind the measurement and the practical limitations of the measurement are not clearly understood.

Although the determination of redox potential is fraught with difficulties, and should not be considered a routine measurement, there are some applications for which at least a relative measurement of the redox potential may prove extremely valuable and the effort may be justified (Nordström and Wilde 2005). Eh measurements (in conjunction with pH measurements) are useful for:

- qualitative insights on groundwater evolution
- qualitative delineation of strong redox gradients, e.g. from artificial recharge or contaminant plumes
- qualitative estimates of the behaviour of multivalent elements in aquifers
- quantitative assessment of iron redox reactions, especially in acid mine waters
- quantitative assessment of sulphide redox chemistry in waters undergoing sulphate reduction

Eh measurements are not useful for quantitative assessment of other redox active species such as methane, bicarbonate, nitrogen, sulphate and dissolved oxygen. These species are not sufficiently electro-active to establish an equilibrium potential at the surface of the platinum electrode (Nordström and Wilde 2005).

4.4.1 ELECTROCHEMICAL THEORY

DEFINITIONS:

Eh is a measure of the equilibrium potential relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode, usually platinum, and an aqueous solution containing electroactive redox species (Nordström and Wilde 2005).
ORP is a less specific term in which the measurements can be made relative to another reference electrode. Voltage measurements obtained as ORP readings can be converted to Eh by adding (or subtracting) the offset voltage of the reference electrode relative to the standard hydrogen electrode.

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. Eh 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. This means that Eh can theoretically be calculated from the activities of the dissolved redox active species. For example, using the oxidation of ferrous iron, the simple half reaction:

$$Fe^{2+} = Fe^{3+} + e^{-}$$

yields the following expression for Eh:

$$Eh = E^{0} + 2.303RT/nF \log (aFe^{3+}_{aq}/aFe^{2+}_{aq})$$

where

- Eh is the equilibrium redox potential (in volts)
- E^{0} is the standard potential if all substances are present at unit activity at 25°C and 1 bar (also in volts: the number is usually looked up from a table).
- n is the number of electrons in the half reaction (in this case 1)
- F is Faraday's constant (96.42 kJ/Volt gram equivalent)
- R is the gas constant (8.314×10^{-3} kJ/mol.deg Kelvin)
- T is the temperature (in degrees Kelvin = °C + 273.15).

- aFe^{3+}_{aq} and aFe^{2+}_{aq} are the thermodynamic activities of the free ions of reduced and oxidised iron in solution, calculated from measured analytical concentrations using an aqueous speciation software program.

The problems of slow redox reactions, non-equilibrium conditions, multiple redox couples and poor interaction of species with the platinum electrode means that the Nernst equation should be used cautiously when interpreting measured Eh.

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).

4.4.2 METHOD OF Eh 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.

4.4.3 Eh EQUIPMENT AND SUPPLIES

An electrometric Eh measuring system consists of:

- the Eh meter
- the measuring electrode
- the reference electrode
- Eh reference solution(s)

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

NOTE: There are several Eh electrodes and combination electrodes on the market which may require slightly different maintenance and operational procedures. Some of the procedures described here may also be out of date if the equipment incorporates more recent technology. Follow the manufacturer's instructions wherever these differ from the procedures described in this manual.

4.4.3.1 The Eh meter

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.

4.4.3.2 The electrodes

The oxidation-reduction indicator electrode is most commonly constructed of platinum, although gold and graphite may also be used. The wax impregnated graphite (WIG) electrode, is more resistant to poisoning and is recommended for very turbid samples (APHA 1998). This section will deal only with the platinum electrode. Consult the manufacturer's documentation for specific instructions of other electrodes.

Eh is defined against the standard hydrogen electrode (SHE), but this is impractical for field use. A reference electrode with a known, stable potential relative to the hydrogen electrode is used as relative reference. The reference electrode is either a silver:silver chloride or a mercury:mercury chloride (calomel) electrode. These are available as liquid or gel-filled electrodes with various types of liquid junction e.g. annular ceramic, quartz or sleeve type.

Eh values are calculated by adjusting for the difference in potential between the hydrogen electrode and the chosen reference electrode. This half-cell potential ($E_{Ag/AgCl}$ or $E_{Hg/Hg2Cl2}$) is dependent on the type of electrode, filling solution concentration and temperature (consult Appendix A.1)

Combination electrodes, which combine the Eh electrode and the reference electrode in one probe are commonly used for Eh measurements. Before use, non-sealed reference or combination electrodes should be filled with the correct electrolyte solution to the level of the fill hole. Make sure that the reference electrode junction is properly wetted.

Electrode performance Unlike the pH measuring system, Eh electrodes cannot be calibrated. The electrode is tested for accuracy using Eh reference solutions, but the slope cannot be adjusted as for pH. The electrode testing procedure with standard solutions is described in the following section.

Electrode maintenance and storage Platinum electrodes may be of foil, wire, ring or billet type (APHA 1998). Keep the metal surface of the electrode brightly polished and clean of coatings or mineral deposits for good performance. A billet tip is more easily cleaned than a wire tip on a platinum electrode (Nordström and Wilde 2005).

Short term storage**:** Immerse the combination electrode in deionised water to above the reference junction and keep the fill hole plugged with a (moistened) rubber sealing ring or with paraffin film to reduce evaporation from liquid filled electrodes.

Store the electrode in saturated KCl solution if recommended by the manufacturer. Separate platinum metal electrodes can be stored in an oxygen-scavenging solution of 0.2M sodium sulphide.

***Long term storage*:** Procedures vary and the manufacturer's instructions should be consulted. Combination electrodes are usually stored dry after rinsing precipitates from the outside of the probe, draining the filling solution chamber and flushing out with water.

4.4.3.3 Eh reference solutions

Eh reference solutions provide stable and known Eh values over a range of temperatures. One of the drawbacks of reference solutions is that they do not cover the range of Eh values found in natural and polluted groundwater, especially in the lower Eh range. Reference solutions can be bought commercially or made up in the laboratory.

The composition of two common Eh reference solutions is given in Table 4.4.1. Use dried salts stored in a desiccator and weigh out accurately for Zobell's solution. Zobell's solution should be stored in a dark plastic bottle in a refrigerator. The solutions should be stable for approximately 3 months. Do not use reference solutions after the manufacturer's expiry date or more than 90 days after preparation, if made up in the laboratory.

Quinhydrone solution has the advantage that by using different pH buffers to make the solution you can cover a wide range of redox potential. Quinhydrone solution is however, less stable than Zobell's solution, especially above 30°C, and its temperature dependence is less well defined (Nordström and Wilde 2005).

Table 4.4.1 Composition of Eh reference solutions.

Reference solution	**Preparation**
Quinhydrone buffer solution Ref: Kokholm (undated)	Dissolve quinhydrone crystals in a suitable acid-base buffer solution (pH 1 to 9) until saturation and then add a few more crystals. The solution contains equal parts of the hydroquinone and quinhydrone redox couple.
Zobell's solution Ref: APHA (1998)	1.4080 g $K_4Fe(CN)_6.3H_2O$ (potassium ferrocyanide) plus 1.0975 g $K_3Fe(CN)_6$ (potassium ferricyanide) plus 7.4555 g KCl (potassium chloride) all dissolved in deionised water and made up to 1L at 25°C. Store in a dark bottle and keep chilled.

Note: Zobell's solution is toxic: handle with care and dispose responsibly.

Temperature dependence Eh is temperature dependant and temperature is therefore important for all measurements. The Eh of the quinhydrone solutions are also pH dependent. The temperature dependence of these reference solutions relative to the standard hydrogen electrode can be calculated from the following equations:

Quinhydrone buffer solution:	$Eh_{,t}$ (in mV) = +700 - 0.1983×(t + 273.15) × pH
Zobell's solution:	$Eh_{,t}$ (in mV) = +428 - 2.2×(t - 25)

where t is the temperature in degrees Celsius.

For ease of reference, the same information for a range of temperatures commonly found in groundwaters is given in Appendix A.2.

The purpose of knowing the Eh potential of the reference solutions at various temperatures is so that you can immerse the container of reference solution in flowing groundwater, equalise and measure temperature and then test the electrode and Eh meter performance all at the sample temperature.

4.4.3.4 Equipment checklist for Eh measurements

(1) Eh meter (or pH meter with millivolt scale)
(2) Eh combination electrode (or platinum electrode and reference electrode)
(3) Eh reference solution (Check expiry date)
(4) 100 mL glass or plastic beaker to hold reference solution
(5) Filling solution for reference electrode (plus syringe)
(6) Electrode cleaning solutions and mild abrasive for polishing
(7) Bucket for equalisation of the reference solution to the sample water temperature.
(8) Thermometer if the Eh meter does not have automatic temperature compensation
(9) Deionised water plus squeeze wash bottle
(10) Soft tissue to dry electrodes
(11) Flat table or working surface
(12) Flow through cell with connectors, tubing and accessories (essential)
(13) Safety equipment and waste disposal containers for working with acid cleaning solutions and Zobell's solution.

4.4.4 FIELD PROCEDURE FOR Eh MEASUREMENT

4.4.4.1 Equipment test procedure

Testing of the performance of the Eh electrode system is time consuming and should preferably be done in the laboratory before and after deployment in the field. If

possible, work at 25°C, as this is the standard temperature for which reference potentials are reported and will simplify any calculations. In general, field testing with reference solutions is not always required, but will depend on the sampling purpose and accuracy requirements. Eh reference solutions may react with dust, small particles of iron from borehole infrastructure or other substances, making field use difficult.

Test the equipment as follows:

(1) Set up the meter and connect the electrodes. Switch on and allow the meter to warm up. If you are working in the field, immerse the container of reference solution in a bucket of flowing sample water to allow for temperature equilibration.
(2) Unplug the reference electrode fill hole. Check the filling solution level and top up to the level of the fill hole if necessary. Shake the electrode gently to remove air bubbles.
(3) Decant a portion of the reference solution into a clean beaker to a level high enough to cover the tip of the platinum electrode and the reference electrode junction.
(4) Rinse the electrode(s) with deionised water and blot dry with soft tissue. Immerse the combination electrode or both platinum and reference electrodes in the Eh reference solution. Do not touch the bottom or the sides of the beaker with the electrodes.
(5) Stir or swirl solution slowly and allow **15 to 30 minutes** for the solution and electrodes to equilibrate.
(6) Rinse the thermometer with deionised water, wipe dry and measure the temperature of the reference solution.
(7) Switch the meter to the millivolt function. Allow the reading to stabilise (± 5 mV fluctuation is fine) and record the millivolt reading and temperature of the reference solution.
(8) Look up or calculate the theoretical potential (E_{ref}) for the reference/electrode system (see below) at the system temperature and compare this to the measured value. If the values are within ±10 mV (some instruments ±20mV even) the equipment is ready for field use. If the values differ by more than that, repeat steps (3) to (7) with a fresh portion of reference solution. If it is still not in agreement, troubleshooting is required (see section 4.4.4.3).
(9) Note the type of reference electrode, type of reference solution and theoretical Eh for the system at the working temperature in your Eh records.

Calculating the theoretical E_{ref} of reference solution

(1) **Eh $_t$** is the theoretical potential of the reference solution relative to the hydrogen; electrode (value from Appendix A.1 or calculated from one of the equations in section 4.4.3.3) at temperature t.

(2) $\mathbf{E_{Ag/AgC,t}}$ or $\mathbf{E_{Hg/Hg2Cl2,t}}$ are the half cell potentials of the electrodes relative to the hydrogen electrode at temperature t (from Appendix A.2).

(3) $\mathbf{E_{ref,\ t}}$ is the theoretical potential of the reference solution for the system being tested; where:

$$E_{ref,\ t} = Eh_{\ t} - E_{Ag/AgCl,\ t} \quad \text{or} \quad E_{ref,\ t} = Eh_{\ t} - E_{Hg/Hg2Cl2,\ t}$$

Appendix A.3 presents a quick reference for E_{ref} values for commonly used electrodes and reference solution combinations over a range of temperatures found in groundwater.

EXAMPLE: Testing a platinum electrode, calomel electrode combination with saturated KCl filling solution with Zobell's solution at 18°C gives a reading of +190 mV. Is the electrode functioning?

The theoretical potential for the system is:

E_{ref} = Eh - $E_{Hg/Hg2Cl2,\ sat\ KCl}$
= (+443 mV) – (+249 mV)
= +193 mV

Eh = +443 mV for calomel electrode with saturated KCl at 18°C (Appendix A.2)

$E_{Hg/Hg2Cl2}$ = +249 mV (Appendix A.1) or

$E_{Hg/Hg2Cl2}$ = -0.66(18) + 261, (Appendix A.1)
= +249 mV.

E_{ref} is within 10 mV of the measured potential, so the system appears to be working properly.

Some meters have a redox calibration function, which requires the theoretical potential (E_{ref}) of the reference solution to be entered by the user. Check whether the value entered is relative to the hydrogen electrode (in which case the instrument automatically compensates for the half cell potential of the reference electrode to calculate Eh) or whether it is relative to the silver:silver chloride or calomel electrode (in which case the ORP readings must be adjusted manually to calculate Eh (see the next section). Setting the reading relative to SHE may cause "out of range" errors on some meters.

4.4.4.2 Field measurements

Eh measurements are sensitive to reactions of dissolved gases and the use of an airtight flow through cell (Chapter 15) is essential. Groundwater samples cannot be preserved for Eh measurements and the readings must be taken in the field. Use an electrode system that has been tested for adequate performance (see section 4.4.4.1).
The steps for field measurement of Eh are as follows:

(1) Check that the reference electrode is filled with the correct filling solution and the platinum electrode is brightly polished.
(2) Rinse the electrodes with deionised water and then with the sample water.
(3) Set up the flow cell with the Eh electrode system and thermometer in place and allow groundwater to run for several minutes to purge air from the cell before taking Eh measurements. Check that the connectors and ports for the sensors do not leak and that the groundwater fills the cell and flows gently eliminating all bubbles.
(4) Switch on the Eh meter and allow it to warm up. If the same meter is used for pH readings, take the pH measurements first and then switch to the millivolt scale for Eh.
(5) Allow the Eh electrode system to reach equilibrium with the groundwater. Note that this may take 30 minutes or more. The platinum electrode should be flushed with large volumes of water to obtain reproducible values. Readings will tend to drift if the water has low concentrations of redox active species or if thermal equilibrium has not been reached.
(6) Take millivolt and temperature readings every few minutes for the first 15 to 20 minutes. Stop the flow while taking readings to avoid streaming potential effects. Record the time, temperature and potential about every ten minutes until at least 30 minutes have passed from the first measurement and the millivolt readings are within ± 10 mV of each other.
(7) Record the reading to the nearest millivolt, noting the plus or minus sign, and the temperature of the groundwater at the time of measurement (to the nearest 0.1°C). Make a note of the reference electrode used.
(8) Calculate the Eh relative to the hydrogen electrode by correcting the millivolt reading for the half potential of the reference electrode (See below).
(9) Rinse electrodes thoroughly with deionised water and blot dry before packing away.

Some natural groundwaters will 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.

To calculate Eh of groundwater:

The steps for Eh calculations are given below with a worked example.

(1) *Using Eh meter with offset function* – when testing the instrument, set Eh reading for reference solution relative to hydrogen electrode (values in Appendix A.2), not relative to reference electrode in use. The difference between the hydrogen electrode and the silver:silver chloride or calomel

electrode will automatically be added to the readings. Eh can then be read directly on the meter.

(2) *Using Eh meter without offset function* – the meter is tested by checking E_{ref} relative to the reference electrode used with the procedure outlined above. The meter reading for the groundwater ($E_{measured}$) must be adjusted to account for the half cell potential of the reference electrode relative to the standard hydrogen electrode. Calculate Eh as:

$$Eh_t = E_{measured,\,t} + E_{Ag/AgCl\,,\,t} \quad \text{or} \quad Eh_t = E_{measured,\,t} + E_{Hg/Hg2CL2,\,t}$$

The subscript $_t$ indicates that all values are unique for the temperature of the water being measured.

The values for $E_{Ag/AgCl}$ and $E_{Hg/Hg2CL2}$ can be looked up in Appendix A.1 for the working temperature of the system.

EXAMPLE: A combination electrode comprising a coupled platinum and silver/silver chloride reference electrode (saturated KCl filling solution) is used to measure Eh of a groundwater sample in a flow-through cell. After 30 minutes, the temperature and millivolt readings stabilise at 22°C and -334 mV, respectively. The instrument does not have an offset function, so the measured potential is relative to the silver/silver chloride electrode and must be converted to Eh.

Eh_t	=	$E_{measured} + E_{Ag/AgCl}$	$E_{Ag/AgCl}$ (+202mV) is interpolated from
	=	(-334 mV) + (202 mV)	Appendix A.1. Using the equation
	=	-132 mV	E = - (22) + 224, gives +202 mV

4.4.4.3 Troubleshooting Eh measurements

There are several reasons why an Eh measurement system may fail to give reproducible readings. Some of the troubleshooting tips below or in the reference documents may help.

If the reference solution does not give the expected theoretical potential:

- check the calculations.
- check the meter and electrodes, as described below.
- use a fresh aliquot of reference solution or make up a new reference solution.

If the millivolt reading does not stabilise:

- check the meter: replace the batteries; use a shorting lead to check the zero reading; check all plugs and connectors; follow manufacturer's instructions for servicing.

- check the platinum electrode: polish the platinum electrode with a mild abrasive; recondition electrode by acid cleaning (aqua regia or chromic acid) as a last resort using the method described below. Poisoned, physically damaged or shorted out electrodes cannot be reconditioned and will need to be replaced.
- check the reference electrode: check that the recommended filling solution has been used; check filling solution level; drain and refill with fresh filling solution; check for an air bubble in the electrode and release it by tapping electrode, swinging by the lead or immerse in warm water to melt KCl crystals trapping bubbles.
- clean the porous pin on combination electrodes.

Platinum electrodes can be cleaned with hydrogen peroxide and detergent washing (use non-phosphate, laboratory grade detergent); anodic activation or abrasive polishing. Polish the electrode with a mild abrasive such as coarse cloth (e.g. crocus cloth), jeweller's rouge, a hard eraser or 400 to 600 grit wet/dry Carborundum^{TM} paper (APHA, 1998)

Noble metal electrodes can, as last resort, be cleaned with strong acid (chromic acid or *aqua regia*):

- *Aqua regia*: make up fresh when required by mixing 1 volume concentrated nitric acid with 3 volumes concentrated hydrochloric acid. Dilute by at least 50% with distilled water; or
- Chromic acid: dissolve 5 g potassium dichromate in 500 ml concentrated sulphuric acid.
- Make up either of the acids and clean electrodes in a fume hood wearing appropriate safety gear. REMEMBER – add acid to water and NOT water to acid. To clean the platinum electrode, immerse in warm *aqua regia* (70°C) for about one minute (not longer or even the noble metal will also dissolve) and then soak for several hours in tap water before use (Nordström and Wilde 2005).

Note: Chromic acid and *aqua regia* are toxic and highly aggressive: handle with care and dispose responsibly. Neutralise acids before disposal.

Combination electrodes should not be fully immersed in strong acid, but the metal tip should still be cleaned and polished. Disassembly of the electrode is not recommended for routine cleaning and should only be used when absolutely necessary (Nordström and Wilde 2005).

A reconditioning procedure for the combination electrode (after Kokholm) is:

- Rinse the surface of the platinum element with conc. H_2SO_4.
- Without contaminating the porous pin, immerse the electrode surface for 10 to 20 minutes in warm (50°C) 3% solution of $K_2Cr_2O_7$ in 10 % (v/v) H_2SO_4.

- Clean the electrode with water and place it in saturated KCl for approximately one hour.

When cleaning a combination electrode, keep the O-ring moist. Remove salt precipitates (KCl from the filling solution) from the outside wall or tip of the probe by flushing with deionised water. The filling solution chamber should also be flushed out from time to time.

To clean the porous pin on combination electrodes (after Kokholm):

- remove *protein* with 5 minute soaking in 5 % (v/v) hypochlorite solution or soak in a strong pepsin solution in 0.1 M HCl for some hours. Rinse with deionised water.
- remove *oil and grease* with acetone. Rinse with deionised water.
- remove *insoluble compounds* (e.g. AgCl) by polishing the porous pin gently with a mild abrasive.
- remove sulphide contamination by sealing the KCl filling hole and soaking the electrode for 24 hours in a solution of thio-urea in 0.1 M HCl. Rinse with deionised water.

4.4.5 REFERENCES FOR Eh MEASUREMENTS

APHA 1998. Standard Methods for the examination of water and wastewater (20th ed), Am. Public Health Assoc, Washington DC.

Appelo, C.A.J. and D.Postma 1996. Chapter 7: Redox processes, 239-295. In: Geochemistry, Groundwater and Pollution. Balkema, Rotterdam.

Hostettler, J.D. 1984. Electrode electrons, aqueous electrons and redox potentials in natural water systems. Am J Sci, 284, 734-759.

Kokholm, G. Not dated. REDOX measurements, their theory and technique (revised edition), Radiometer A/S, Copenhagen, Denmark.

Lindberg, R.D. and D. Runnells 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modelling, Science 225, 925-927.

Nordström, D.K. and F.D. Wilde 2005. Reduction-oxidation potential (electrode method), U.S. Geological Survey, Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.5, (version 9/2005). Available from the URL: http://pubs.water.usgs.gov/twri9A6/ (last accessed on 22 November 2006).

Stumm, W. and J.J. Morgan, 1996. Chapter 8: Oxidation and reduction equilibria and microbial mediation. In: Stumm, W. and J.J. Morgan, Aquatic Chemistry (3rd ed), John Wiley & Sons, New York, 425-515.

Thorstenson, D.C. 1984. The concept of electron activity and its relation to redox potentials in aqueous geochemical systems. U.S. Geological Survey Open-File Report 84-072, 45p.

Whitfield, M. 1974. Thermodynamic limitations of the use of the platinum electrode in Eh measurements. Limnol. Oceanogr. 19, 857-865.

4.5 DISSOLVED OXYGEN

The maximum quantity of oxygen that can dissolve in water is proportional to the local atmospheric pressure and inversely related to water temperature and salinity (Figures 4.5.1, 4.5.2 and 4.5.3). In low-salinity water at sea level, the dissolved oxygen (DO) content of water saturated with air is 9 mg/L at 20^{o}C. Only in waters subject to high photosynthetic rates, will the DO level ever exceed that of air-saturation.

Dissolved oxygen has a significant effect upon groundwater quality since it regulates the valence state (and thus the solubility) of many trace metals and by constraining the bacteriological metabolism of organic compounds in groundwater (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 main characteristic of oxygen is its ability to oxidise (that is, accept electrons from) other species in water (Stumm and Morgan 1996). Both electrons and energy are transferred in biological and geochemical oxidation-reduction (redox) reactions. No other naturally occurring constituent of water is a more energetic, or biologically reactive, oxidant than molecular oxygen; therefore aerobic bacteria utilize DO as part of their metabolism. This results in the oxidation of organic carbon, hydrogen sulphide, ammonium and other reductants. An important aspect of these biochemical redox reactions is their irreversibility. *Bacterial metabolism always consumes, but never produces oxygen.*

Dissolved oxygen concentration is a critical parameter in any investigation of groundwater contamination, particularly those involving the migration of landfill leachates or mining wastes. Oxygen in water often controls the fate of dissolved organic contaminants by constraining the types and numbers of micro organisms present within an aquifer. In turn, bacteria can either decompose or, in some cases, produce organic contaminants as part of their metabolism. For example, most alkyl benzene and chloro-benzene groups are probably biodegradable in aerobic water while they are stable in anaerobic water. Conversely, trichloroethylene (TCE) is stable in oxygenated water while possibly biodegradable in anaerobic water.

A detailed investigation of contaminant migration from landfills, tailings piles and retention ponds should define a three-dimensional DO profile within both the contaminant zone(s) and the surrounding region. The often-mapped parameters TDS and EC usually cannot be used to infer the presence or concentration of oxygen-sensitive contaminants such as methane or hydrogen sulphide. The dissolved organic carbon (DOC) concentration in landfill leachate is often hundreds of times higher than that in uncontaminated groundwater. When groundwater becomes polluted to this degree, DO is likely to be absent, even at shallow depths. However, this assumption always requires site-specific verification.

Oxygen, in large part, influences the solubility of many naturally occurring, polyvalent trace elements in groundwater. Nine of the 16 inorganic constituents that have specified concentration limits in drinking water in the USA (As, Cr, Fe, Hg, Mn, Se, U, N, S), have multiple oxidation states and are therefore sensitive to DO concentration. Other potentially hazardous heavy metals (Ag, Cu, Cd, and Zn) form ionic complexes and solid compounds with multivalent elements, notably sulphur. The concentrations of these heavy metals are therefore also influenced by DO in water. Uranium, selenium, and arsenic are insoluble under reducing or anaerobic conditions. Conversely, iron and manganese are insoluble in aerobic water (with a neutral pH). The pH of the solution and the concentration of inorganic and organic complexing agents need also be considered in determining the fate of these species.

DO 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.

4.5.1 METHODS OF DO MEASUREMENT

4.5.1.1 Method selection

The methods available for DO determination are:

- **Winkler** (iodometric) titration which is a cumbersome method that is seldom used anymore.
- **Amperometric** measurement through a membrane (DO electrode), which is the common field method. This is the preferred method of analysis because of its simplicity.
- **Spectrophotometric** determination in which the sample is added to an ampoule of chemicals and the colour change is measured with a spectrophotometer or compared with tests samples or a colour chart. The Rhodazine D technique can have a lower detection limit than the electrode method (Lewis 2006, White et al. 1990).

Table 4.5.1 shows a comparison of the merits of different DO analysis methods. The electrode method will be described in detail. Details of the spectrometric method can be found in the instrument suppliers' literature and the USGS manual (Lewis 2006). Details of some semi-quantitative field methods are given in section 4.7 (*field test kits*).

Table 4.5.1 Comparison of DO methodologies (White et al., 1990, and Chemetrics 2006).

	DO electrode	Spectrophotometric with field spectrophotometer	Spectrophotometric with colour comparator
Initial costs	High	Medium	Low
Running costs	Low	High	High
Level of understanding required	Low if sufficiently automated	Medium	Low
Minimum detection level	0.1mg/l	0.01mg/l	0.01mg/l
Calibration required for mg/l measurements	Yes	No	No
In-flow analyses	Yes	No	No
Interference	H_2S	Oxidizing agents	Oxidizing agents

4.5.1.2 DO electrode method

The detector of the DO meter is a polarographic system consisting of two metal electrodes surrounded by an electrolyte (Wood 1981; APHA 1998). When a suitable polarizing voltage (usually 0.8 volt) is applied across the cell, the consumption of oxygen at the cathode causes a current to flow through the cell. This current is directly proportional to the oxygen consumption rate. The electrode system is separated from the test solution by an oxygen-permeable membrane. The membrane (polyethylene or fluorocarbon) serves as a diffusion barrier against impurities, but is transmissible to oxygen. The rate at which oxygen diffuses through the membrane is proportional to the pressure differential across the membrane. Since all the oxygen is immediately consumed at the cathode, the current through the electrode system is then proportional to the oxygen diffusion rate through the membrane, which is itself proportional to the absolute pressure of oxygen outside the membrane. Suitable two-point calibration procedures are used to convert this current to a DO measurement.

The critical parts of the electrode system are, the membrane which can easily get damaged or fouled with contaminants, and the electrodes which accumulate products from the oxygen consumption reaction. Successful field measurements require proper sampling to ensure sample integrity, stability of the instrument readings and proper calibration to convert instrument readings into meaningful DO results,

4.5.2 EQUIPMENT AND SUPPLIES FOR DISSOLVED OXYGEN

4.5.2.1 Sampling devices suitable for DO analysis

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 acceptable (Table 4.5.2). The rule is that no air should 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 4.5.2 Sampling pumps suitable for monitoring dissolved oxygen (from Rose and Long 1988).

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 well below the spring orifice
Production well (pump in place) pumping	Conditionally acceptable as a method of last resort	Intake level should be well 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 well 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

4.5.2.2 Checklist of dissolved oxygen equipment

(1) DO meter and electrode (with spare membranes, O-rings and electrolyte)
(2) Flow-through cell, preferred especially for low-DO water
(3) Thermometer (if not included in the DO meter)
(4) Barometer (if not included in the DO meter)
(5) Two 250 mL plastic bottles
(6) One 1000 mL plastic bottle for aeration of reference sample or manufacturer's aeration flask.

(7) 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.

4.5.3 FIELD PROCEDURE FOR DISSOLVED OXYGEN MEASUREMENT

The electrode only provides a relative DO reading and should be calibrated before each use. The procedure consists of checking whether the zero point is correct and then calibrating the high DO end of the electrode by using a sample of known DO content (air saturated with water).

The procedure below describes all the steps required to do this absolute calibration. Modern instruments automate some of these steps. It is essential for the user to understand the level of sophistication of his/her instrument to avoid double correction to the measurements.

The diffusivity of a Teflon® membrane changes by 3% per ^{o}C. The temperature at which the measurement is done is therefore crucial. If your instrument/electrode is not equipped with a temperature probe, be scrupulous with the temperature settings between samples.

4.5.3.1 Zero point calibration

A deoxygenated water sample is produced by a solution of sodium sulphite (10g $Na_2S_2O_3$ per litre plus a trace of cobaltous chloride). The steps to determine this point are as follows:

(1) Pour a sample of the groundwater into a 250 mL plastic bottle. Add several mL of the zero DO solution. Replace cap and stir. This is the de-aerated sample.

(2) Prepare the DO meter for calibration according to manufacturer's instructions.

(3) Switch the meter to the DO reading position. Insert the electrode in the de-aerated sample of Step 1. The DO reading should be less 0.02 mg/L.

(4) If the DO reading is greater than 0.02 mg/L, add saturated sodium sulphite in small increments until a reading <0.02 mg/L is obtained. Add an excess of several ml to ensure low DO in the water. If this can not be achieved, then clean the electrodes or replace the membrane before continuing.

4.5.3.2 High point calibration

The high end of the scale requires a measurement of water with a known DO concentration.

Make sure you understand the term "automatic correction of….." of your instrument. It may mean that the instrument is equipped with a sensor that detects the property in question (temperature is an easy one) and applies the required correction. It may also mean that the user should enter the required value (e.g. altitude, barometric pressure and/or salinity) after which the instrument will do the required correction. So please make sure you understand every button and knob on your instrument before leaving for the field. This you do by reading and understanding the manufacturer's manual.

The usual high-point calibration method is to place the electrode in a bottle with air at 100% moisture content. Use sample water, especially in high salinity cases. Most DO instruments are supplied with an equilibration flask, containing a sponge that can be wetted, into which the electrode is inserted. An alternative is to make a bottle of air-saturated water by shaking water in the presence of air or having air bubbled through the water.

(1) Pour a sample of the groundwater into the equilibration flask and insert the electrode. Alternatively use a 1 L plastic bottle and aerate for 15 minutes by shaking vigorously after which you should pour an aliquot of the aerated sample into a clean 250 mL plastic bottle and insert the electrode.

(2) Switch the DO meter to the DO setting position and allow the meter to settle. If required, set the pressure and temperature dials to the correct values.

(3) For a fully automated (pressure and temperature) meter, calibration will now be complete and the setting can be stored. The meter is now ready for use.

(4) For a non-automated system you should calculate the DO concentration of the aerated sample, by taking the water temperature, the barometric pressure (alternatively elevation) and the salinity into account. Follow steps 5-9.

(5) Use the water temperature to obtain the solubility of oxygen in water in mg/L (Figure 4.5.1).

(6) If a pressure reading on site is available, read off the pressure correction factor (Figure 4.5.2); otherwise use the site elevation (in masl from Figure 4.5.3).

(7) If EC > 200 mS/m then read off the salinity correction factor from Figure 4.5.4.

(8) Multiply the solubility with the two correction factors to obtain the corrected value.

(9) Adjust the DO reading with the calibration control to the value obtained by step 8. Some instruments will allow you merely to set “% saturation” to 100%. The meter is now ready for use.

To get the pressure input correct, note that
1 atmosphere = 760 mm Hg = 101 325 Pa = 1013 hPa = 1013 mBar

To improve the calibration accuracy, the tables of Appendix B.1, B.2 and B.3 can be used, rather than figures 4.5.1 to 4.5.4.

Example calculation of saturated DO:
At 22^{o} C and 1400 masl and EC = 4000 mS/m ;
DO of water saturated with air will be:
8.7 * 0.845 * 0.86 = 6.3 mg/L = 198 µmole/L

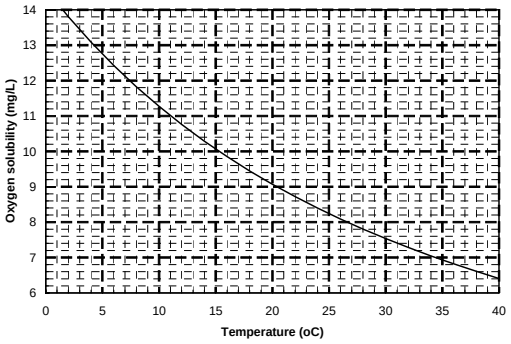

Figure 4.5.1 Solubility of oxygen from saturated air as function of temperature (from Weiss 1970).

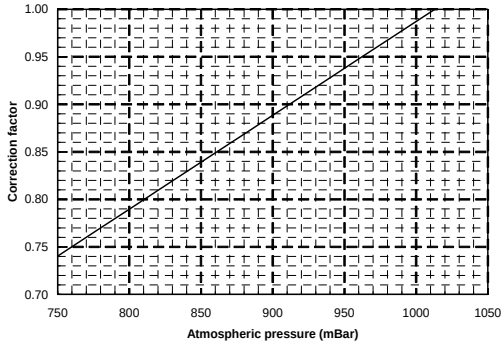

Figure 4.5.2. Correction factor to account for reduced atmospheric pressure on oxygen solubility.

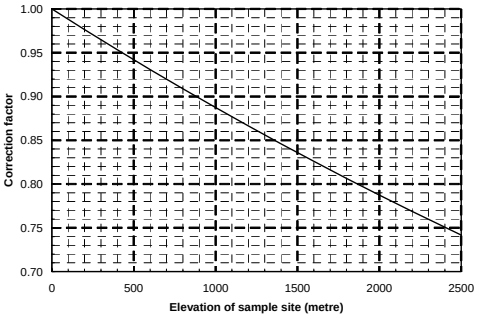

Figure 4.5.3. Correction factor to account for reduced air oxygen solubility at higher elevations.

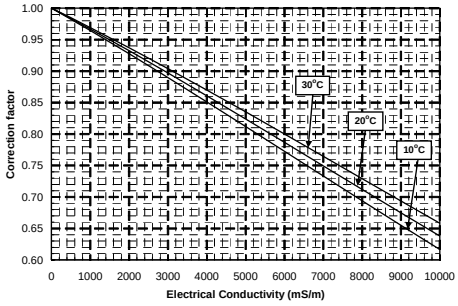

Figure 4.5.4. Correction factor to account for salinity effects on oxygen solubility (from Weiss 1970).

4.5.3.3 Measurement of DO

Actual DO measurement of the sample water can be done once the meter/electrode system has been calibrated. A well looked after electrode will remain stable during a day's work provided the water temperature remains constant. It is nevertheless good practice to check the high-point calibration at every site. The analysis procedure with a calibrated system is as follows:

(1) Place the sensor in the flow-through cell. Gently open the flow control valve.

(2) 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. It is important not to have too high a flow-rate, otherwise a pressure effect will be introduced which will give erroneous readings.

(3) Record the meter reading to the nearest 0.1 mg/L.

(4) Dismantle and wash the equipment with distilled water.

(5) Store the electrode according to the manufacturer's instruction. This usually means that the membrane tip of the electrode be kept moist.

ALWAYS measure Dissolved Oxygen in a flowing stream of water: NEVER use discrete samples.

4.5.3.4 Trouble shooting

- In case of malfunction, first check the battery and the integrity of all the connections to the electrode.
- Re-do both calibration steps.
- If the low-point calibration value has shifted, electrode cleaning is usually required
- If the high-point calibration value has changed, then the fault usually lies with damage to the membrane. Replace the membrane and recalibrate the electrode.

4.5.4 DO REFERENCES

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

Chemetrics 2006. URL: http://www.chemetrics.com/home.html. (last accessed on 17 October 2006).

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

Lewis 2006. Chapter 6.2, Dissolved Oxygen, U.S. Geological Survey, Techniques of Water-Resources Investigations, book 9, chap. A6., section 6.2, (version 6/2005). Available from the URL: http://pubs.water.usgs.gov/twri9A6/ (last accessed on 22 November 2006).

Rose, S. and A. Long 1988. Monitoring dissolved oxygen in groundwater: some basic considerations. Ground Water Monitoring Review, 8(1), 93-97.

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.

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

4.6 ALKALINITY AND ACIDITY

If the investigation requires an understanding of the chemical equilibrium related to carbonate minerals, it is essential to obtain accurate values of pH and the carbonate and bicarbonate concentrations of the groundwater. In such cases, either conducts a total alkalinity determination (titration) in the field, or else, measures 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 at the borehole on a fresh sample.

Investigations requiring field alkalinity measurements will include:

(1) Hydrogeochemical studies in aquifers with high carbonate e.g. dolomite and coastal quaternary sands.

(2) Water stabilization investigations including:
- water-softening
- water-conditioning to reduce cement aggressiveness
- water-conditioning to reduce cast iron and mild steel aggressiveness
- iron and manganese removal
- management of carbonate encrustation.

(3) Certain pollution investigations.

(4) Sampling for radiocarbon isotopes.

The formal definition of the alkalinity of water is its acid neutralising capacity. Total alkalinity is the sum of all titratable bases in the sample (APHA 1998). For most groundwaters 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.

The practical implementation is that a sample is titrated to a designated pH value, generally the equivalence point (between pH 4 and 5) of the weak acid-base carbonate system: $CO_2 – HCO_3^- – CO_3^{2-}$ (Loewenthal et al., 1986).

When the pH of the water sample is above pH 8.3, alkalinity titrations are conducted to two endpoints*.

- The first end-point (around pH 8.3) is used to determine **carbonate alkalinity** (phenolphthalein alkalinity)

* The terms ‘end point’, ‘equivalent point’ and ‘infection point’ used in titration discussions all have the same meaning.

- The second end-point (around pH 4.5) gives **bicarbonate alkalinity** (methyl orange alkalinity).

Acidity is the lesser used opposite parameter to alkalinity. It is the quantitative capacity of water to react with a strong base to a designated pH value (APHA 1998). Acidity is quantitatively linked to the corrosion potential of water. It is sometimes reported as 'negative alkalinity'. The endpoint needs to be specified: usually it is pH 8 or 9.

4.6.1 THE CARBONATE SYSTEM IN WATER

Carbon dioxide, bicarbonate and carbonate in groundwater originate from a variety of sources (atmosphere, plants, soil and aquifer material). The reactions that relate these species to pH in natural waters are:

$$CO_2 + H_2O <=> H_2CO_3 <=> HCO_3^- + H^+ <=> CO_3^{2-} + 2H^+$$

Lower H^+ (higher pH) tends to shift both reactions to the right. The equations can be used to show the distribution of the different carbonate species in water as affected by pH (Fig 4.6.1). At pH<5 there is only dissolved CO2 in solution, between pH 5 and 10 bicarbonate dominate and at pH>10 all of it is in the carbonate specie. Alkalinity (as sum of $HCO_3^- + CO_3^{2-}$) only becomes significant above pH 4 and doubles in value beyond pH 9. Within the range of pH 6 and 10 alkalinity is therefore a fair measure of bicarbonate concentration.

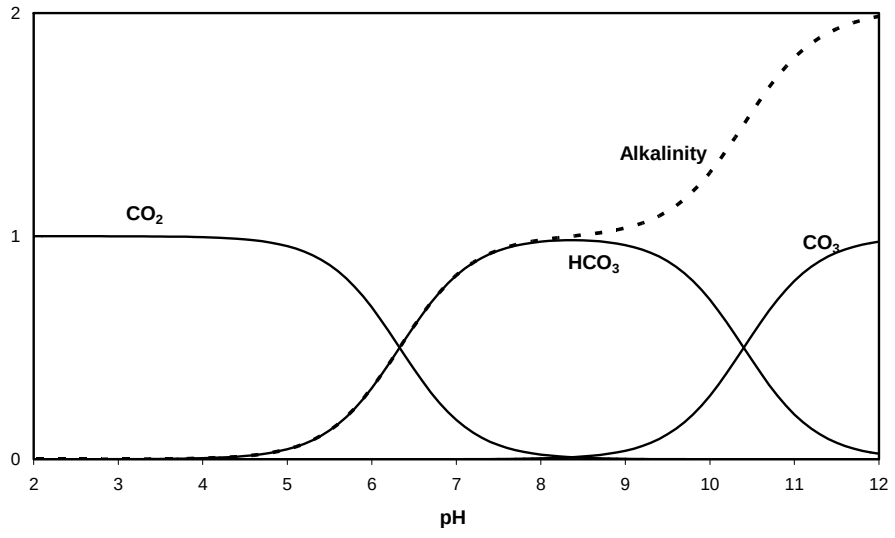

Figure 4.6.1. Distribution of CO_2, HCO_3^-, CO_3^{2-} and alkalinity as a function of pH (Loewenthal et al., 1986). The y axis shows the relative concentration in mmol/L (and meq/L for alkalinity).

A titration curve (Fig 4.6.2) shows the pH response to the addition of acid to a sample. Inflection points of the curve (also called "titration endpoints") are the

characteristic pH value where the most rapid pH change occurs. The first one is the point where all the carbonate has been converted to bicarbonate (near pH 8: fig 4.6.2) and then again when all the bicarbonate has been converted to CO_2 (near pH 4: fig 4.6.2) (APHA1998: method 2320B, Rounds 2006). The aim of titration in the field is to perform the titration procedure with sufficient care and then to determine the inflection point(s) with the accuracy required for the task in hand.

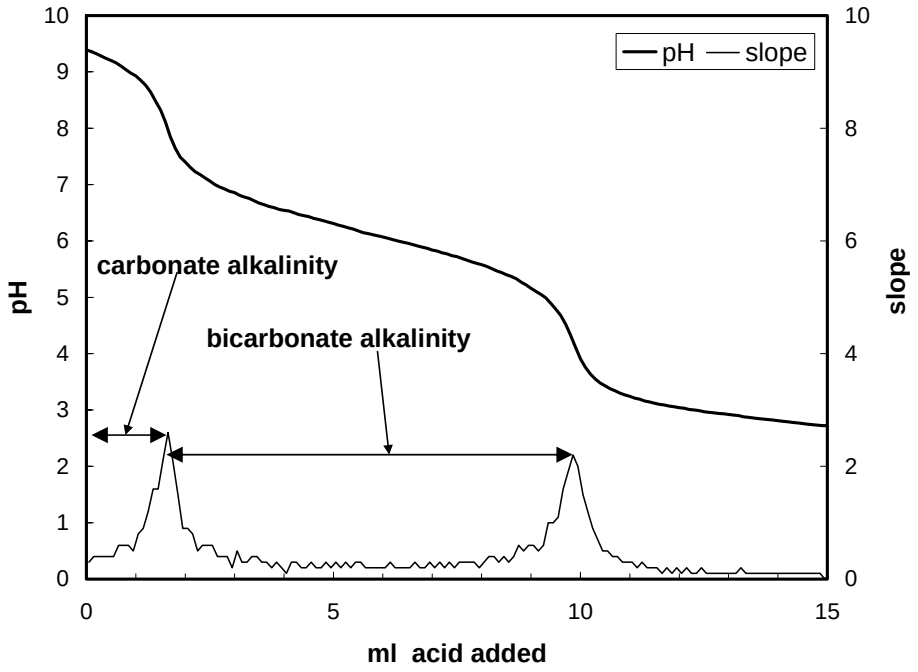

Fig 4.6.2 Typical titration curve of a somewhat alkaline, unpolluted water sample. The upper curve shows the pH change as function of quantity of acid added. The lower curve shows the calculated slope (=ΔpH/ΔV).

4.6.2 TITRATION METHODS

Alkalinity and acidity determinations involve the titration of a quantity of sample with acid (or alkali for acidity) in order to determine the quantity of acid necessary to reach one or both inflection points. The main requirements are to prevent loss or gain of CO_2 and to detect the endpoint precisely enough.

The simplest (and classic) endpoint determination is by using **colour indicators** that are used to show pH changes (Table 4.7.1). In general, indicator alkalinity determinations in the field are less precise than proper laboratory titrations, even if done days later. pH indicator titration is described as one of the short-cut methods in chapter 4.7.

The use of a **pH meter** to determine the endpoint is a more precise method because it allows better definition of the end points. It is the method of choice for general field

practice. Modern pH meters are robust enough to be used in the field (see chapter 4.3 *pH*) and together with a magnetic stirrer can provide accurate titration results. The method would be either to read off the inflection point pH and note the corresponding acid volume, or to use a graphic method to determine the inflection point (Rounds 2006). The inflection method requires a set of regularly spaced additions and corresponding pH values. The acid volume at which a maximum pH response per acid volume added, is obtained, indicates the inflection point (Figure 4.6.2). This evaluation can be done in the field using manual or small spreadsheet methods. There is even a web page available on which the required calculations can be done (Rounds 2003).

The **Gran method** of end point determination is based on using the behaviour of the curvature of the titration curve on either side of the inflection points (Gran 1952, Stumm and Morgan 1981, Rounds 2006, 2003). This approach is only recommended for special cases where alkalinity and/or EC are low or where there are significant non-carbonate interfering species present.

Establishment of the infection points with a pH meter is the recommended method for alkalinity determination. Usually one needs to setup and calibrate the pH meter anyway for pH measurements. With good care this method provides sufficient accuracy for most purposes and should be better than transporting samples to a laboratory for titration days or weeks later. While it is better practice to analyse samples directly at the sampling point, it is quite often acceptable to accumulate all the samples during the day, keep them cool and do all the titrations in a field lab at the end of the day. This is, however, not recommended for samples with either very low or very high pH because of possible CO_2 interaction with air.

4.6.3 TITRATION EQUIPMENT

The equipment recommended for field titration is:

(1) pH meter, buffers and glassware for pH measurement (see chapter 4.3)
(2) 25 mL burette
(3) 25 or 50 mL pipette
(4) magnetic stirrer and stirrer bar
(5) stands, clamps, 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
(9) a well-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.

4.6.4 PROCEDURE FOR ALKALINITY AND ACIDITY DETERMINATION

4.6.4.1 Field titration

The titration procedure is as follows:

(1) Set up the burette, pH meter and magnetic stirrer.
(2) Calibrate the pH meter with buffers (section 4.3).
(3) Rinse the burette with a small quantity of acid (of molarity M_1).
(4) Rinse a beaker and stirrer bar with distilled/deionised 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 (see figure 4.6.2).
(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 (Fig 4.6.2).
(12) Determine the end point (V_1) by one of two methods:
(13) Visually establish the value of V at which the pH changed most rapidly
(14) A more precise alternative to (13) is to calculate the slope ($\Delta pH/\Delta V$) for each interval, plot it against V (as in Fig 4.6.2) and determine the points of maximum slope.
(15) The calculation of alkalinity is done by the following equation:
   a. $Alk = M_1 \times V_1/V_2 \times 1000 \times 50$ (in mg $CaCO_3$/L)
(16) Rinse the beaker and pipette. Discard unused acid from the burette and pack everything away.

CALCULATION 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 the course of time, it will become evident which pH values are critical for endpoint determinations and only readings in restricted pH ranges need to be taken (usually 9 - 8 and 5 - 4).

Under 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. Write down each time you add a measured volume of acid and record the pH after gently swirling the beaker by hand. Start using the larger volume pipette (e.g. 1 ml) and then change to a smaller volume (e.g. 0.1 ml) as you approach the end point. With this method it is very important to keep good track of the acid additions so that you can calculate the total volume added.

4.6.4.2 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 buret. 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 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 mg$CaCO_3$/L or meq/L. Unpolluted water with high CO_2 content (low pH) needs to be handled with care to minimize CO_2 loss. Water polluted by other acids is less fragile.

4.6.4.3 Alkalinity and acidity units

Alkalinity and acidity concentrations are usually reported as mg$CaCO_3$/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 4.6.2). The conversion formulae are as follows:

1 meq alkalinity =	50 mg $CaCO_3$ =	61 mg HCO_3^- =	30 mg CO_3^{2-}

Many 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 (see Figure 4.6.1) 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), the bicarbonate concentration.

For waters with pH between 4 and 9, carbonate and bicarbonate concentrations can be calculated from the pH and total alkalinity (TA) (APHA 1998: method 4500-D):
If TA is expressed in mg$CaCO_3$/L, then

$$B = HCO_3 \text{ (mg/L)} = 61/50*(TA - 5*10\text{^}(pH-10))/(1 + 0.94*10\text{^}(pH-10))$$

and

$$C = CO_3 \text{ (mg/L)} = 0.56*B*10\text{^}(pH-10)$$

Geochemical speciation models can be used for more detailed calculations.

4.6.5 ALKALINITY AND ACIDITY REFERENCES

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

Gran, G. 1952. Determination of the equivalence point in potentiometric titrations. Analyst 77, 661.

Loewenthal, R.E., H.N.S. Wiechers and G v R. Marais 1986. Softening and stabilization of municipal waters. Monograph, Water Research Commission, Pretoria.

Rounds, S.A. 2003. Web-based Alkalinity Calculator. URL: http://or.water.usgs.gov/alk/ (last accessed 17 October 2006).

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).

Stumm, W, and Morgan, J.J. 1981. Gran titration, Appendix to Chapter 4. Aquatic Chemistry, 226-229, J Wiley & Sons, New York. 780p.

4.7 FIELD TEST KITS AND OTHER SHORT CUT METHODS

There are a number of simple test kits available on the market that can be used to test for specific determinands in water at the borehole and obtain immediate results. The results may not always be very accurate, but they do enable one to make a yes/no decision in the field. They are thus a very useful item as they can result in significant time and cost savings during pilot sampling or when large changes of a substance are expected in a monitoring project. The methods employed range from various colour methods, to drop titrations, to field colour comparison, and to electrometric methods. The method of choice depends on the accuracy requirements, anticipated frequency of use, skills of the operator and cost.

Most of these methods are short-cuts of established laboratory techniques and imply that the user is not as well protected against interferences from other constituents as a proper accredited laboratory method will be. Measurements made with these methods in the filed need to be backed up by proper laboratory analysis later.

4.7.1 COLOUR METHODS

Colour responses of combinations of chemicals are well known and actually form the backbone of many accredited standard laboratory methods. The intensity of colour is related to concentration. Some of these methods have been adapted for simple routine measurement.

4.7.1.1 Indicator Strips

Indicator papers (also called test sticks) are well-known for pH measurement and used for quick checks. Various papers are available covering different ranges and sensitivities down to 0.5 pH units. Many other determinands in water can be analysed in a similar way with specific papers. The paper is wetted with the water sample, some time is allowed for development of the colour and it is then compared with a colour chart. In some cases, e.g. NH_4, another reagent needs to be added first. The papers are generally not suitable for low concentrations and may be influenced by other major constituents. Merck supplies a wide range of papers trademarked Merckoquant®), Sigma-Aldrich supplies Quantofix® test sticks, and there are other suppliers.

4.7.1.2 Visual Colour Comparisons

Accuracy and sensitivity of colour indicators are improved when the reaction takes place in a flask of sample and thereafter colour comparisons are made. In these cases some indicator and/or reagent is added to a quantity of sample water in a tube and it is compared to a colour chart. This is the well-known method for free chlorine and pH testing in swimming pool water. Various levels of complexity are available that are useful for groundwater professionals (e.g. Aquamerck®, Aquaquant® and Microquant® of Merck, Chemets® of Chemetrics, Aquanal® of Sigma-Aldrich, and

others). The variations provide for longer path length to improve sensitivity or colour comparison to enable turbid or coloured waters to be analysed. These methods require more experience, cleanliness of work area, good light and some cost for the purchase of indicators.

4.7.1.3 Field Spectrophotometry

Upscaling of the visual comparison of colours requires an instrument (also called a colorimeter) to measure colour intensity more reproducibly. Small battery-powered units exist, into which a sample tube can be inserted for analysis. Generally some standard is required and this has to be taken on site and the instrument calibrated before use. Methods exist to accommodate coloured or turbid water. Suppliers known to the authors are Merck (Reflectoquant®), Hanna, Chemetrics, Sigma-Aldrich (Aquanal®).

4.7.2 FIELD TITRATIONS

For some determinands (e.g. hardness and alkalinity) no colour tests exist and titrations in the field need to be done. The field alkalinity method using a pH meter described in chapter 4.6 provides quite accurate results. Simple kits are available that yield semi-quantitative results that may be acceptable in some cases. With titration one is not looking at intensity of colour as in the above examples, but at a colour change when the equivalence point is reached. Titrations basically require a fixed volume of sample, an indicator and some sort of dispenser to control and measure the reagent added. Light levels and water colour should be sufficient to observe the colour change at the equivalence point.

Different indicators with different colours are available (Table 4.7.1). The HTH® test kit commonly available in South Africa for swimming pool water testing uses bromo-cresol green as indicator for alkalinity determination. A sample volume of 16 mL is measured out in the supplied special plastic container. Acid (0.06N) is dispensed with a dropper (each drop ≈ 0.05 ml) and the colour change observed. The alkalinity (as $mgCaCO_3/L$) is obtained by multiplying by 10 the number of acid drops used to reach the endpoint. The precision of this method is hardly better than 20%, but there may be occasions where this can be acceptable (e.g. radiocarbon sampling where one needs to determine sample size, see section 3.3.3).

Table 4.7.1. pH indicators suitable for alkalinity determination (from Vogel 1951)

Indicator	pH range	Low pH colour	High pH colour
methyl orange	3.2 - 4.4	red	Yellow
bromocresol green	3.8 - 5.4	yellow	Blue
phenolphthalein	8.2 - 0.0	colourless	Pink
thymol blue	8.0 - 9.6	yellow	Blue

The Merck system (Aquamerck®) and the Hanna system both use droppers to add reagent into plastic vials. The Chemetic system (Titrets®) uses a syringe-type holder with an ampoule of reagent.

4.7.3 ION SELECTIVE ELECTRODES

Electrodes have been developed that produce specific responses (in mV) for certain anions and cations in water (Rundle 2006). Similarly to pH and Eh, it is therefore possible to connect such an electrode to a pH meter or a special millivolt meter. After calibration this yields the concentration of that determinand in water: usually a logarithmic response to concentration. These electrodes can be influenced by interfering substances and are fragile. Orion Research were the pioneers in the development of ion selective electrodes, but there are now other manufacturers as an internet search will show.

4.7.4 H_2S STRIP FOR COLIFORMS

A simple method has been developed to indicate coliforms in water. This consists of a treated material in a sterile plastic vial. Water is added and the vial closed and left standing at room temperature for up to 72 hours. A black colour indicates the presence of coliforms. A limitation is that if H_2S is present then a positive is always obtained. Fortunately the human nose is extremely sensitive to H_2S (rotten egg), so these false positives can mostly be avoided. The kits are quite inexpensive (between R10-R20).

Sobsey and Pfaender (2002) reviewed many variations of the H_2S strip test. Genthe and Franck (1999) tested the method and its application in South African rural water supply projects and are now recommending the method and selling built-up kits. Mosley and Sharp (2005) describe the method and production of kits from common chemical supplies. Although the kits are simple to make, their version can also be purchased. HACH chemical company make a H_2S test called the Pathoscreen test. It is described as Bacteria: Hydrogen Sulphide Producing, Method 10032, for the detection of: Salmonella, Citrobacter, Proteus, Edwardsiella, Klebsiella (some spp). Cost is R200 per test.

4.7.5 REFERENCES

Rundle, C.C. 2006. A Beginners guide to ion selective electrodes: URL: http://www.nico2000.net/Book/Guide1.html (last accessed on 22 November 2006).

Genthe, B. and M. Franck. 1999. A tool for Assessing Microbial Quality in Small Community Water Supplies: an H_2S Strip Test. Water Research Commission Report 961/1/99, Pretoria, 33p.

Mosley, L.M. and Sharp D.S. 2005. The hydrogen sulphide (H2S) paper-strip test. A simple test for monitoring drinking water quality in the Pacific Islands. South Pacific Applied Geoscience Commission (SOPAC) Technical Report 373. Suva, Fiji. URL: http://www.sopac.org/data/virlib/TR/TR0373.pdf (last accessed on 17 October 2006)

Sobsey, M.D. and Pfaender F.K. 2002. Evaluation of the H_2S method for the detection of fecal contamination of drinking water. World Health Organization. Report WHO/SDE/WSH/02.08. Available from the URL: http://www.who.int/water_sanitation_health/dwq/wsh0208/en/index.html. (last accessed on 17 October 2006)

Vogel, A.I. 1951. Quantitative Inorganic Analysis, Longmans Green, London. 918p.

4.7.6 SUPPLIERS OF EQUIPMENT

The authors do not claim that the supplier's list is complete, nor can they guarantee the performance of the products

Chemetrics: http://www.chemetrics.com/ (last accessed on 17 October 2006)

CSIR H_2S Strip Test. Ms M Franck, CSIR, Stellenbosch, South Africa. Ph 021 888 2581, Fax 021 888 293, mfranck@csir.co.za.

Hach Pathoscreen test. URL: http://www.hach.com/hc/search.product.details.invoker/PackagingCode=2859100/NewLinkLabel=PathoScreen+Field+Kit (last accessed on 17 October 2006)

Hanna: URL: http://www.hannainst.com/ (last accessed on 17 October 2006)

Merck: URL: http://photometry.merck.de/servlet/PB/menu/1168630/index.html (last accessed on 17 October 2006)

SOPAC H_2S paper-strip test. Institute of Applied Sciences, University of the South Pacific, Box 1168, Suva, Fiji. Ph: (679) 3212967, Fax: (679) 3300373. URL: http://www.sopac.org/data/virlib/TR/TR0373.pdf (last accessed on 17 October 2006)

Orion (now part of the Thermo Corporation). URL: http://www.thermo.com/com/CDA/Category/CategoryFrames/1,2213,248,00.html (last accessed on 17 October 2006)

Radiometer (ion selective electrodes) URL: http://www.radiometer-analytical.com/news/en_electrode_catalogue.asp?s=go (last accessed on 17 October 2006)

Sigma-Aldrich: http://www.sigmaaldrich.com/Brands/Fluka___Riedel_Home/Analytical/Analytical_Specialties/AQUANAL_reg_.html (last accessed on 17 October 2006)

CHAPTER 5

DOWN-HOLE LOGGING FOR FIELD DETERMINANDS

5.1 INTRODUCTION

Field measurements are usually taken from flowing boreholes using a bucket or flow-through cell at the wellhead. Thanks to the advances in sensor technology, down-hole logging instruments have been developed that can be used to take physical and chemical measurements inside the borehole. These can be used for measuring unstable determinands in the aquifer with minimal disturbance, since no pumping is required. They are also useful for plotting vertical profiles of how determinands vary with depth, which can be used to interpret contaminant plume movement, water quality stratification or flow characteristics. A very good understanding of how the borehole is constructed, which sections are screened or open hole, is essential when interpreting the data.

Geophysical “wireline” logging is a fairly well-established practice, which traditionally includes limited water quality determinands, such as temperature or electrical conductivity. Several other types of down-hole sensors are now available. These have expanded water quality logging capabilities to include pH, dissolved oxygen, Eh and even some dissolved ion concentrations, such as ammonium, chloride or nitrate, in addition to temperature and electrical conductivity (Hydrolab 1997).

In simple down-hole logging systems, a long cable probe is lowered down the borehole connected to the meter and power source, which remain at the surface. This method has been in common use for electrical conductivity logging using a 'low loss' or impedance matched cable. It tends to be impractical, however, for working at depths of more than about 50 metres.

Modern down-hole logging instruments usually combine four to six different sensors in one submersible multi-probe. The sensors are attached to a submersible data logger with on-board power source. The whole unit is watertight and pressure rated to 20 bar or more (currently instruments up to 150 bar are available). This allows the logger to be lowered down the borehole on a rope to depths of up to 200 or 300 metres below surface. The data logger is programmed in advance to take readings at specified time intervals. Data is then retrieved by downloading to a computer after retrieval from the borehole. Systems are also available where data can be transmitted via telemetry. For vertical profiling, depth is measured by a pressure sensor (below the water table) or using graduations on the rope used to lower the logger.

Downhole logging offers a useful addition to routine and specialised groundwater investigations by adding information about the vertical dimension in aquifers.

5.2 CALIBRATION AND MAINTENANCE OF LOGGING EQUIPMENT

Downhole logging instruments are sophisticated devices, which are usually supplied with a comprehensive instruction manual as well as software for programming the data logger or downloading data (for example Hydrolab 1997). In most respects the procedures for maintenance, calibration and troubleshooting of the individual sensors are similar to those described in Chapter 4 on field measurements.

To identify possible problems, check the sensor calibration in the office or laboratory on the day before heading out to the field. Some suppliers provide a multipurpose standard solution which allows several parameters (e.g. EC, pH, and Eh) to be calibrated at once.

- Electrical conductivity readings should be checked against a standard conductivity solution (chapter 4.2).
- At least two pH buffer solutions should be used to calibrate the pH electrode, with the buffers chosen to bracket the pH expected range of the groundwater (e.g. pH 7 and pH 4 or pH 7 and pH 10) (chapter 4.3). Calibration of the pH meter should be checked again once in the field by measuring the pH of the buffers and recalibrating if necessary immediately before logging.
- Eh electrodes should be checked with a standard redox buffer solution (see chapter 4.4) and the platinum electrode cleaned if the Eh reading is not in agreement with that of the standard.
- Check that the dissolved oxygen membrane is not fouled and that the probe can be calibrated before leaving for the field (chapter 4.5). Dissolved oxygen calibration is sensitive to atmospheric pressure and the instrument must be recalibrated at the sampling site. Most dissolved oxygen sensors require some agitation of the water sample (e.g. flowing water) and a stirrer is used on some loggers to fulfil this function.
- Follow the manufacturer's instructions for calibrating ion sensitive electrodes if you are planning to use these on your logger.
- Some instruments have pressure sensors to measure depth, which should be zeroed under atmospheric pressure conditions at the sampling site.

Because logging devices are lowered down boreholes, the probes tend to become more easily fouled than other field equipment and require proper cleaning after each sampling trip. Use only the tools, cleaning materials and detergents or solvents recommended by the manufacturer.

Periodic visual inspection of the instrument, comparison of pre- and post-calibration results and monitoring of sensor response time can be used to decide when maintenance or servicing is required. Regular maintenance procedures may include:

- Filling or replacing reference electrode filling solution. Check that you use the correct concentration of KCl.
- Replacing the dissolved oxygen membrane.
- Cleaning the platinum Eh electrode.
- Replacing components such as o-rings for sealing the instrument.
- Replacing worn rope or damaged cables immediately.

Loggers tend to use more power than traditional field meters and replacing batteries or recharging the power supply is also a common maintenance activity. Checking the power supply is the first option for troubleshooting. Batteries should be removed when the logger is in storage.

If batteries or probes are replaced, or any part of the logger is opened for some other reason, be careful to ensure that the watertight seal is restored and all electronic components are protected against water leakage. Water-repellent grease, such as silicone grease, may be used to ensure a good seal if advised by the manufacturer.

5.3 HELPFUL HINTS FOR OPERATION OF DOWN-HOLE LOGGERS

It is not possible to provide detailed step-by-step instructions on the use of down-hole logging devices because there are several different instruments on the market, which operate in different ways. It should also be noted that at the time of writing, down-hole logging is a growing field in groundwater studies and the information in this manual may be out of date. This section gives some general advice which should be applicable for down-hole chemical logging of boreholes.

- First check the water table by measuring with a water-level probe, and total borehole depth. The borehole depth must be known from data sheets, do not plumb the bore to measure depth, as you will disturb stratification. This allows you to determine an appropriate depth interval for readings and estimate how long the logging is likely to take.
- Try to take at least two readings at each depth, before lowering the logger by the next increment, to check the reproducibility of the results.
- At the start of logging, once the logger is submersed in the borehole, hold it for a few minutes below the water table. This is to allow time for the sensors to stabiles. The response of the Eh and dissolved oxygen sensors, in particular, is sometimes sluggish and can give an inaccurate impression of the depth of aeration of the water if not allowed to equilibrate.
- Lower the logger smoothly and slowly between measurements to avoid stirring up the water column.
- Stop the logging at least 1 or 2 metres above the bottom of the borehole. There is usually a sump constructed at the base of a

borehole which collects mud, sand, biofilm and other materials that form or fall into the hole. These can cause unnecessary fouling or damage to the sensors.

- We have found that readings taken when the logger is raised quickly out of the borehole often fail to agree with those from when slowly lowering the instrument. Disturbance of the water column and inadequate equilibration times are possible reasons for this observation. In general, any data collected while pulling the logger out of the borehole should be rejected.
- Pumping of the borehole before logging or pumping of nearby boreholes during logging can have a large impact on the vertical profile data. Stratification of water quality in the aquifer cannot be identified under such conditions (Tredoux et al., 2000). It is probably safest to allow at least one day with no pumping before trying logging the borehole.
- Down-hole logging devices are expensive and are exposed to unusual risks when lowered into the subsurface. Protruding pieces of screen or casing along joints, changes in casing diameter or foreign objects in the borehole can provide obstacles that damage the logger or cause it to become lodged in the borehole, particularly in cases where boreholes are poorly constructed. Sometimes borehole logs are also inaccurate, for example the depth may not be properly recorded. To minimise risks to the logger, a dummy can be used. This is simply a cylinder, preferably of slightly bigger dimensions and greater mass than the logger, which is lowered down on a rope to check the ease of access before logging, especially in unfamiliar boreholes. The time needed to stabilise after disturbance of the water column by the dummy must be weighed against the considerable expense of damaging or losing the logger.

5.4 A CAUTIONARY NOTE REGARDING DOWN-HOLE LOGGING

Down-hole logging data can provide very useful insights to water quality variations with depth and this relation to either lithological changes, or to fracturing. Down-hole loggers should be used more often in groundwater quality investigations.

A cautionary note is however raised. Down-hole loggers by their very nature need to be used in boreholes that are “open-hole”. Thus the data must always be interpreted with due regard for the misleading results that can be introduced by vertical flow in the borehole. This is discussed in more detail in section 16.3 *Limitations of open borehole techniques.*

5.5 REFERENCES

Hydrolab 1997. Datasonde® 4 and MiniSonde® Water Quality Multiprobes. User's manual, Revision D. Hydrolab Corp, Austin, Texas.

Tredoux, G., Cavé, L.C. and Engelbrecht, J.F.P. In-situ measurement of physico-chemical parameters down a borehole as a tool for resource evaluation. In: Sililo et al. (eds). Groundwater: Past Achievements and Future Challenges. Proceedings of the XXX IAH Congress, Cape Town, 26 Nov - 1 Dec 2000. AA Balkema, Rotterdam. 667 – 672.

CHAPTER 6

QUALITY ASSURANCE

6.1 INTRODUCTION

Quality assurance (QA) is a set of operating principles which, if strictly followed during sample collection and analysis, will produce data of known 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. If the QA is good and correct, the analytical results cannot be rejected as being invalid by a court of law.

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 accurately as possible. Analytical results are only as good as the samples they are testing.

Sixteen items should be included in a QA plan, and they can be grouped together as follows (Keith and Wilson 1982):

A: Format
- (1) title page
- (2) table of contents

B: Project overview (what is the purpose of the project?)
- (3) project description
- (4) project organization and responsibility

C: Data quality objectives (what will be required?)
- (5) QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability

D: Measurement activities (how will it be done?)
- (6) sampling procedures
- (7) sample custody
- (8) calibration procedures and frequency
- (9) analytical procedures
- (10) data reduction, validation, and reporting
- (11) internal quality control checks and frequency
- (12) preventive maintenance

E: Quality assurance (can the results be trusted?)
- (13) performance and systems audits and frequency
- (14) specific routine procedures to be used to assess data precision, accuracy and completeness of specific measurement parameters involved
- (15) corrective action
- (16) quality assurance reports to management.

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 sixteen 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 organized around the major headings listed above might be in order. Many of these items are also included in the Monitoring Programme Guide (Chapter 7) which is an information file taken into the field by the sampler.

6.2 QUALITY CONTROL

Discussed in this section are the specific internal quality control methods that should be followed. Section 6.3 (*Quality Assessment*) describes the external quality control methods. For the field scientist collecting groundwater samples, the following items must be considered.

- Use buffer and standard solutions which are the same temperature as the groundwater being sampled to calibrate field chemistry meters. Calibrate before a field measurement and if possible after the field measurement is complete. Make notes in your field notebook that these calibrations have been done.
- Send a **duplicate sample** with the set of samples to the laboratory. Collect twice as much sample from the same borehole, and decant 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).
- A **laboratory blank** is either a sample of deionised water or deionised water plus the reagents depending on the analytical method. If you are collecting VOC samples take a trip blank with you.
- A **trip blank** is water known to contain no hydrocarbons placed in two of the sample bottles. These are carried in the cooler bag in the field and returned to the laboratory with the samples. The trip blank is analysed at the same time as the field samples. This is to ensure that external VOCs did not contaminate the groundwater samples.
- When the same sampling pump is used for several pollution monitoring boreholes, collect an equipment blank (also called field blank). Choose one of the boreholes showing the highest level of contamination, decontaminate the sampling equipment (Chapter 18), and then collect a sample of the final rinse water as an equipment blank.
- Ensure that **quality control standards** are used by the analytical laboratory. A quality control standard is a typical sample of known constitution which is included with every set of samples that they analyse. Most laboratories use quality control standards as part of their internal QC program. If your laboratory does not have/use a QC standard, either change laboratory or prepare your own standard. On the pilot sampling run, fill a 20 L container

with groundwater from a borehole which is representative of the area. Allow the sample to stabilise for 2 - 3 weeks, filter and then include a sample from the drum with every set of samples submitted. Obviously fragile parameters such as nitrate, alkalinity, many organics etc cannot be checked in this way.

There are further internal Quality Control checks which are carried out by the laboratory and which do not form part of the field sampling methodology and thus are not included in this manual. However, the manager of a groundwater monitoring program must be aware of them, especially should litigation occur. Read about them in APHA (1998) and in Canter et al. (1987).

6.3 QUALITY ASSESSMENT

Quality assessment is external QC. This is a performance audit which is carried out periodically to determine the accuracy of the measurement system. Modern rapid analytical techniques are capable of giving very precise results, sometimes at the expense of accuracy. It is not uncommon in a monitoring programme which samples boreholes at regular intervals over a period of time to encounter changes in groundwater chemistry when a change in analyst or laboratory occurs. Quality assessment includes such items as performance evaluation samples, performance audits and inter-laboratory comparison samples.

In South Africa, the South African National Standards (SANS) conducts a nation-wide inter-laboratory comparison study called SANS Water-Check. This programme is open to participation by all laboratories that analyse water and wastewater samples. Use only a laboratory that regularly participates and is accredited. Inter-laboratory comparison for organic compounds is conducted by SANAS. Isotope inter-laboratory comparison surveys are conducted by IAEA.

Performance audits should be carried out on field sampling techniques on an unscheduled basis. The procedure involves using a check-list to document the manner in which a sample is collected and delivered to the laboratory. The goal is to detect any deviations from the standard operating procedures so that corrective action can be taken. Design the audit for the monitoring programme and include in the QA plan (Item 13, Chapter 6.1). For further reading see APHA (1998) and Canter et al. (1987).

6.4 REFERENCES

APHA 1998. Standard Methods for the examination of water and wastewater (20th ed), Am. Public Health Assoc, Washington DC.

Canter, L.W., R.C. Knox and D.M. Fairchild 1987. Ground Water Quality protection. Lewis Publ, Michigan.

Keith, S.J. and L.G. Wilson 1982. Stacking the deck in ground water quality data. Proceedings of the Arizona Section, American Water Resource Association Ground Water Quality Symposium.

CHAPTER 7

MONITORING PROGRAMME GUIDE

7.1 INTRODUCTION TO WATER QUALITY MONITORING

Water quality monitoring is the systematic and careful collection and analysis of samples, observations and *in situ* measurements with the aim of providing an information and knowledge about a water body (ANZECC 2000).

Fig 7.1 (ANZECC 2000) shows the components of a monitoring programme. The important point is that this is an interactive process, so that at all times the objectives of the programme are kept in mind and the programme re-assessed 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.

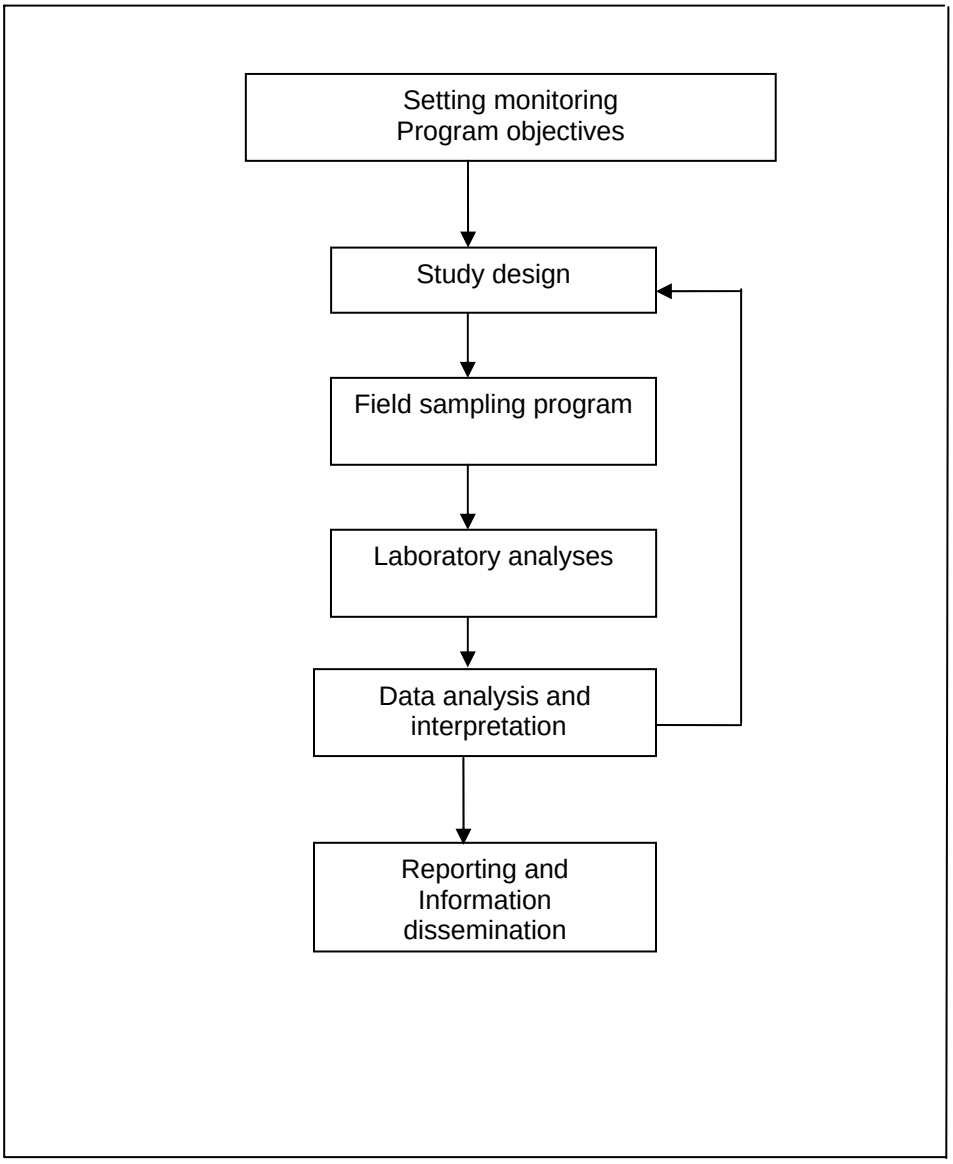

Figure 7.1. Framework for a water quality monitoring programme (from ANZECC 2000)

This groundwater sampling manual is not intended to describe in fine detail the methods of developing a monitoring programme as in Fig 7.1. It is rather a description of the methods within the part of the programme described as "field sampling methods" in Fig 7.1. There are a number of documents discussing the design of monitoring programmes. Amongst these the following two should be referred to "Design of networks for monitoring water quality" (Sanders et al*.,* 1983) and "Australian guidelines for water quality monitoring and reporting" (ANZECC 2000).

Things to be considered by the designers of the monitoring programme are: effective sampling, significant parameters, laboratory requirements, cost, time and efficiency. Each programme should be specifically designed and, on occasion, deviate from normal sampling procedures to achieve a better end-result. Liaison with the laboratory is of paramount importance and the designer should work hand in hand with laboratory managers. Pilot sampling runs are vital to detect possible initial sampling errors and to develop a smooth running groundwater monitoring programme.

7.2 MONITORING PROGRAMME GUIDE

This is a very important part of any groundwater sampling programme, as the guide describes in detail the information needed by staff to locate the correct groundwater sampling point and to collect the water sample in a manner that is exactly the same as the previous sampling run, and exactly the same as the next sampling run. This is done to ensure that the method of sample collection does not introduce an error in the analytical result. If, for some very valid reason, there is a change of sample collecting procedure, this must clearly be documented. Such a procedural change may introduce a change in the analytical results, and unless there is a clear record, the observed change may be interpreted as a change in subsurface conditions.

The monitoring programme guide consists of three parts

(1) The master guide which is kept in the office
(2) The field file which has a set of relevant information which is needed in the field
(3) Sample records and chain of custody forms (this is dealt with in more detail in the next chapter)

7.2.1 MONITORING PROGRAMME (MASTER) GUIDE

This document is kept in the office, so that if some mishap should occur to the field crew, this document can be referred to and copied, and a replacement sampling crew

can continue with the sampling programme with no interruption. It will contain the following:

- A description of the project and what aims of the project the sampling programme is likely to achieve.
- The same information as described below for the Monitoring Programme Guide
- The field data sheets from previous sampling runs. Copies of these are inserted into the Field guide
-

7.2.2 MONITORING PROGRAMME (FIELD) GUIDE

This is the document taken into the field by the sampling crew. It is referred to at all times to check that the correct site is being sampled and is being sampled correctly. It must include the following:

- A detailed list of the equipment needed to carry out the sampling run. See chapter 2.5 for a comprehensive sample equipment checklist.
- Calibration and checks to field instruments that need to be done before departure from the base.
- Safety information.
- Map(s) showing the location of each borehole and/or sampling site. A detailed small-scale map is often necessary for individual boreholes, especially if there is more than one borehole at the site.
- Where to obtain keys for gates and borehole locking caps.
- Contact details about the owner and supervisor(s) of the site.
- Contact details of the contact person who provides access to the site.
- Local contact person in case there is a problem.
- Depth and size of the borehole(s) to be sampled. It is expensive to arrive at a site with a sampling pump too large to fit in the borehole.
- Position of screens or fractures, i.e. position for installing sampling pump and/or packers.
- Rate of discharge and pumping time to purge the borehole correctly. Note that the first field sampling run will set the discharge and pumping times for subsequent sampling runs. However the field sampler must still perform field measurements and if there is significant diversion from previous results, then use discretion and purge accordingly. This variation must be recorded and discussed with the program supervisor.
- Field measurements to perform at each borehole.
- Number and type of samples to collect at each borehole.
- Procedure for preserving and sending samples to the laboratory.
- Any other data, however trivial, that may be of importance, e.g. distance to pollution source, distance to nearest pumping borehole, etc.

A Monitoring Programme Guide should be a carefully compiled document which is the result of experimentation in the field and laboratory. By spending time and effort designing a sampling programme, a lot of unnecessary work can be avoided.

A Monitoring Programme Guide should also include:

- A plan or chart of the project organisation showing the line of authority of key personnel.
- Anticipated starting and completion dates.
- Intended use of acquired data.
- The name of the responsible person in the laboratory who is the sample custodian authorised to sign for incoming samples.
- Schedule of preventative maintenance tasks which will ensure smooth running of sampling.
- A list of critical spare parts which should be on hand.
- A plan for periodic assessment of data accuracy, precision and completeness.

7.3 REFERENCES

ANZECC 2000. Australian guidelines for water quality monitoring and reporting, National water quality management strategy No 7a, published by the Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand. URL: http://www.deh.gov.au/water/quality/nwqms/monitoring.html (last accessed on 17 October 2006)

Sanders T.G., R.C. Ward, J.C. Loftis, T.D. Steele, D.D. Adrian and V. Yevjevich 1983. Design of networks for monitoring water quality, Water Resources Publications, Littelto, Colorado. ISBN 0-918334-51-9

CHAPTER 8

SAMPLE RECORDS AND CHAIN OF CUSTODY

8.1 INTRODUCTION

The Monitoring Program Guide (Chapter 7) describes in detail the information needed by staff to collect samples consistently from one sampling run to the next. Complementary to this Guide is the requirement 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 are 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 SHEET

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 program. 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, many, if not most, from the various Government Agencies from each of the States of the USA. A few of these are included at the end of this chapter.

The contents of a field record sheet usually comprise the following:

General data

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

Sampling site data

- 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.
- Sample ID recorded on bottle and on Chain of Custody form.
- Borehole physical data: Any damage; depth to water surface, depth to bottom of borehole; calculate water level above sea level.
- Sampling pump details: Type; depth of intake; pumping rate; required purging, time to purge;
- Field determinands: 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.
- Sampler's observations on the pumped water: Colour and colour changes during pumping; odours; DNAPLs or LNAPLs.
- Sample handling: Filtering; sample bottle type and size; preservatives; storage.
- Provide space for additional notes at the end of the sheet.

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

8.3 CHAIN OF CUSTODY

There will be occasions when the results of a groundwater monitoring program will be entered 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 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.

The following *Field Chain of Custody Procedures* have been adapted from the Wisconsin Groundwater Sampling Manual (Karklins 1996):

(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.

8.4 WEB ADDRESSES FOR FORMS

Wisconsin Home site
http://www.dnr.state.wi.us/org/water/dwg/gcc/Pubdwnld.htm (last accessed on 5 November 2006)

Sampling document
http://www.dnr.state.wi.us/org/water/dwg/gw/pubs/field.pdf (last accessed on 5 November 2006)
http://www.dnr.state.wi.us/org/water/dwg/gw/pubs/desk_a.pdf (last accessed on 5 November 2006)
http://www.dnr.state.wi.us/org/water/dwg/gw/pubs/desk_b.pdf (last accessed on 5 November 2006)

US EPA OSWER- 9950.1 This publication, entitled the RCRA Ground- Water Monitoring Technical Enforcement Guidance Document (TEGD), describes in detail what the United States Environmental Protection Agency deems to be the essential components of a groundwater monitoring programme. **Note this is a 10 MB document**. URL:

http://www.epa.gov/Compliance/resources/policies/civil/rcra/rcragwguiddoc-rpt.pdf (last accessed on 5 November 2006)

ANZECC 2000 Australian guidelines for water quality monitoring and reporting, http://www.deh.gov.au/water/quality/nwqms/monitoring.html (last accessed on 5 November 2006)

Chain of custody, US Geological Survey. This document deals with COC for geochemical samples (not water), nevertheless it contains some good descriptions and has a form. http://pubs.usgs.gov/circ/1997/c1138/c1138.htm (last accessed on 5 November 2006)

The Minnesota Pollution Control Agency has a variety of COC forms on their website at http://www.pca.state.mn.us/water/groundwater/sampleguide.html (last accessed on 5 November 2006)

Cyto Labs
http://www.cytoculture.com/sample%20info.htm (last accessed on 5 November 2006)
http://www.cytoculture.com/generic%20AN%20CC.doc (last accessed on 5 November 2006)

8.5 REFERENCES

ANZECC 2000. Australian guidelines for water quality monitoring and reporting, National water quality management strategy No 7a, published by the Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand http://www.deh.gov.au/water/quality/nwqms/monitoring.html (last accessed on 5 November 2006)

Karklins S.1996. Groundwater sampling field manual. PUBL-DG-038 96, Bureau of Drinking Water and Groundwater, Wisconsin Department of Natural Resources, Madison, Wisconsin. http://www.dnr.state.wi.us/org/water/dwg/gw/pubs/field.pdf (last accessed on 5 November 2006)

CHAPTER 9

SAMPLE CONTAINERS AND SAMPLE PRESERVATION

9.1 SAMPLE CONTAINERS

The container for collecting and storing the water sample must be selected bearing the following in mind: resistance to solution and breakage, efficiency of closure, size, shape, availability and cost. The two commonly used container materials are polyethylene or PVC plastic and borosilicate glass.

Glass: This must be borosilicate glass and preferably a dark colour to reduce photo degradation of the sample and growth of biological matter. Where possible, polyethylene plastic bottles should be used as glass can break in transit or in the laboratory which means a repeat sampling trip. Glass is not suitable for boron, silica and sodium analyses. Glass is the best container for organic constituents and the only container for DO analyses.

Plastic: Either polyethylene or polyvinylchloride (PVC) plastic bottles can be used. Polyethylene is preferred as less adsorption occurs on it than on PVC. Plastic bottles are preferred to glass for general drinking water samples due to their resistance to breakage. Plastic bottles must not be used for DO and for organic compound analyses. Plastic bottles only should be used for silica and boron analyses.

9.2 SAMPLE BOTTLE PREPARATION

Sources of error could arise if sample bottles are not properly prepared before a sampling run. New bottles must be rinsed, filled with water and allowed to soak for several days to remove any water soluble compounds. The bottled water industry uses food-grade PET plastic bottles which are specially designed not to have leachable substances in the plastic. With the world-wide increase of consumption of bottled water over the past 10 years, these bottles are freely available and, as long as the bottles are new, can be used without preparation for most sampling exercises. For specialised analyses such as heavy metals and organic compounds the sample bottle preparation is more involved. Each section of Chapter 3, *Determinand Selection*, has a paragraph on sample bottle preparation which must be strictly and routinely adhered to in order to produce consistent results.

9.3 MARKING THE SAMPLE BOTTLE

Nothing is more frustrating than returning from a sampling trip to find that the sample number and field data have been washed off or rubbed off. To prevent this happening, the best method is to use a waterproof felt-tip pen to write on sample

bottle labels and then cover the writing with a clear adhesive tape. (3M 72 mm wide transparent tape works well).

The bottle label should include the following:

- Sample ID no
- Sample site and borehole number
- Date and time of sampling
- Field parameters (pH, Eh, DO, T and alk)
- Whether filtered or not filtered
- Whether preservative has been added, and what type of preservative.

9.4 SAMPLE PRESERVATION

Sample preservation methods are intended to retain the collected sample as close as possible to its original state in the underground environment. Preservation methods are intended to:

- retard biological activity
- retard chemical reaction
- reduce volatility.

Methods are limited to:

- pH control
- chemical stabilizers (HNO_3, NaOH, $HgCl_2$ etc.)
- refrigeration
- freezing.
- poisoning

No matter which method is applied, complete preservation is not possible and it is good practice to analyse as soon after sampling as is practical. Confirm with the laboratory what the analysis turn-around time is before submitting samples. If the delay is too long, consider changing laboratories. Proper sample handling which includes preservation reduces sampling error which in turn increases the accuracy and thus effectiveness of groundwater monitoring. Preservatives and their actions are detailed in Table 9.1 below. Specific requirements are listed in Appendix C.1.

Table 9.1 Various preservatives that may be used to retard changes in samples

Preservative	Action	Applicable to
Refrigeration	Bacterial inhibitor	Acidity - alkalinity, organic materials, BOD, colour, odour, organic P, organic N, carbon, etc., biological organism (coliform, etc.)
Acid (HNO_3)	Dissolves metals, prevents precipitation	Metals

Acid (H_2SO_4)	Bacterial inhibitor Salt formation with organic bases	Organic samples (COD, oil and grease, organic carbon) Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
$HgCl_2$	Bacterial inhibitor	Nitrogen forms, phosphorus forms

Mercury compounds are being phased out as preservative because of the health hazard and the possibility of heavy metal contamination.

9.5 SAMPLE SIZE

The golden rule is to ask the analytical laboratory what volume of water sample they need before going into the field. If you have omitted this detail, rather collect twice as much as you think necessary - it's a lot cheaper and less time-consuming than having to go back for a top-up sample.

It is also good practice to use a number of smaller sample bottles for one sampling site rather than one large bottle. For example, the chemical laboratory at CSIR used by the authors requests 3 x 330 mL bottles for the major cations and anions, One bottle is used for the analysis, the second bottle is used if there is a problem during the analysis (e.g. the cations and anions do not balance and the analysis has to be repeated) and the third bottle is stored for a few months after the analytical results have been posted in case of any queries concerning the analysis.

CHAPTER 10

WATER-LEVEL MEASUREMENT

10.1 INTRODUCTION

When arriving at a borehole or well to collect a water sample, the first measurement that must be taken is the water-level and the second is the depth of the borehole. However if you intend to use the low-flow sampling method or down-hole logging method, then measure the depth after sampling is complete. By lowering the dip meter probe to the bottom of the borehole you disturb sediment that has settled, and this will create turbidity and thus require a longer purging time.

There are a number of reasons why the water-level and the depth of the borehole must be measured, amongst others.

- If the water-level measuring device cannot go down the borehole, the sampling pump will also not be able to go down.
- When sampling an unknown borehole, the depth of installation of the sampling pump must be determined. If the borehole has been sampled previously, the depth measurement will indicate whether borehole collapse or silting has occurred.
- The volume of water that must be purged (see Chapter 13) must be calculated so that a representative sample can be collected.
- Water-levels are essential for calculating groundwater flow directions and seasonal changes of the aquifer.

10.2 WATER-LEVEL MEASURING EQUIPMENT

10.2.1 The Dip-meter

The apparatus of choice is a twin-core cable mounted on a hand-winch (Figure 10.1). This tool is called a dip-meter. The end of each wire is bared so that the open contacts are ~50 mm apart (Figure 10.2). A weight is hung below the bared ends. The weight must be stainless steel, not lead or copper, as these latter will introduce contamination. At the top end, the circuit is completed with an indicator such as an ohm or milli-amp meter (using a multi-meter), a buzzer or a light.

When the bared ends are submersed in the water, either the ohm meter or amp meter needle deflects or the buzzer buzzes or the light lights up. This system can quite easily be made up in a workshop. They are also freely available from most suppliers of groundwater monitoring equipment.

Figure 10.1 Hand-winch and twin-core cable set-up, fitted with a voltmeter for water level measurement. The 6 volt battery fitting for the voltmeter is dangling next to the voltmeter

Figure 10.2 Close-up of the probe at the end of the cable showing the upper bared end and the lower end soldered to the metal weight.

To measure the depth to water-level use one of the following three methods:

(1) Securely attach the zero of the measuring tape at the upper open contact and lower the tape with the twin core cable. If the tape is to be left as a permanent fixture on the water level measuring equipment use a fibre glass tape as a steel tape will rust. This is the method of choice.

(2) Permanently mark the cable at 1 m intervals and measure the final part of the last metre with a carpenter's tape. This method is less preferred as the cable can stretch. Also, errors can be made when adding or subtracting the partial metre to or from the last noted whole metre.

(3) Mark the cable, remove it from the borehole and measure the depth of the mark with a tape. This method is not preferred as it requires two persons.

10.2.2 Measuring in a 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 well-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 piping usually used is class 4 or 6 HDPE irrigation tubing. 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.

A water level measuring device that is useful for equipped boreholes which do not have such piezo-tubes fitted, is a sonic water-level meter. This can “see” past the riser-main, cabling and other fittings. Its accuracy is about 0.2% of the depth to the water level, but the readout accuracy is 0,025 m. It is however a fairly expensive item (compared to the dip meter), costing about R7000.

10.3 FIELD PROCEDURE

10.3.1 Field procedure – general monitoring boreholes

(1) Lower the sensor of the dip meter down the borehole or the piezo-tube until the needle deflects, the buzzer or light goes on. Raise it until it stops deflecting or going off. This is the water-level.
(2) Measure the water-level depth using the datum point, which should be marked on the casing, usually the top of the casing.
(3) Re-check the water-level and record.
(4) Lower the weight until the bottom of the borehole is felt and record the depth. Has siltation occurred since it was last measured? Record the data.
(5) Note that lowering to the bottom of the borehole will disturb the water column and dislodge particles that are loosely attached to the sidewall. If the borehole is to be purged, i.e. the borehole has a reasonable yield of water; this may not affect the sample integrity. However for low-yielding boreholes for which purging may not be done, then rather first collect the water samples and measure the depth of borehole after completion of sample collection.
(6) Remove the cable and clean off any rust or oil.

10.3.2 Field procedure – pollution monitoring boreholes

(1) If the borehole being sampled is a pollution monitoring borehole, then due consideration must be taken as to the suitability of the materials that will come into contact with the contaminant water. Can these be properly cleaned? Refer to Chapter 11 for a detailed discussion on materials.
(2) If each borehole is properly purged and sampled in order i.e. from least to most contaminated, the risk of cross-contamination will be minimized, and there is no need to decontaminate your water level cable until the final borehole. If not, then clean it thoroughly before doing anything else.
(3) If floating NAPLs, such as hydrocarbons are present, these will coat and prevent the simple electrical device as described above, from working properly. If LNAPLs are suspected to be present, or are the reason for sampling, then a specially designed water level meter must be used. This

measures both the water level, plus the thickness of the LNAPLs. These can be purchased from specialist suppliers.

(4) An alternate measuring device is a “plopper”. This is a smallish cup-shaped weight, attached to the measuring tape. This is lowered and when the down-pointing cup touches the water or NAPL layer a “plop” is heard. This is repeated a few times to be sure the correct liquid level is being measured. A small brass bell with the clapper removed works well (Stainless steel SS316, would be preferred, as the brass may introduce contaminants).

(5) The sonic water level meter mentioned in section 10.2.2 above, has the advantage that using it will reduce the danger of cross-contamination.

CHAPTER 11

SAMPLE COLLECTING DEVICES

11.1 SAMPLE COLLECTING DEVICES

The following article by Pohlmann and Hess (1988) is reprinted verbatim and with permission from Groundwater Monitoring Review Vol. 8 No.4. Although nearly 20 years old the sampling tools have not changed significantly, and this review paper is regarded as being comprehensive and complete. The only notable changes in groundwater sampling technology are the concept of low flow sampling, and the use of foot valve samplers. These are discussed at the end of the reprint. Some minor additional notes and comments have been added at the end of the reprint. For this revised manual the units of the original article have been converted to S.I. units.

Generalized Ground Water Sampling Device Matrix
by K.F. Pohlmann and J.W. Hess

The sampling matrix was prepared by K.F. Pohlmann and J.W. Hess of the Water Resources Center, Desert Research Institute, University of Nevada System, and submitted to the U.S. EPA as part of a cooperative research program. The chart is based on a review of the literature, and it illustrates general relations of ground water parameters to sampling devices. There were 12 types of sampling devices and 14 ground water determinands (including inorganic, organic, radioactive, and biological) considered, and notes regarding sampling depths, well diameters, sample delivery rates, and construction materials were included.

The matrix was prepared in response to ground water sampling research needs expressed by the U.S. EPA Regional and Program Offices and is one part of EMSL-LV's continuing Comparative Testing of Ground Water Sampling Methods research project.

Description of Sampling Devices and Construction Materials Commonly Used

***Open bailer - Open top**. Bottom sealed or fitted with foot valve. Available in wide range of rigid materials.*

***Point-source bailer** - Check valve at both top and bottom. Valves are opened by cable operated from ground surface. Available in wide range of rigid materials.*

***Syringe sampler** - Sample container is pressurized or evacuated and lowered into sampling installation. Opening the container and/or releasing the*

pressure allows sample to enter the device. Materials may include stainless steel 316, Teflon®, polyethylene, glass.

Gear-drive pump *- Electric motor rotates a set of Teflon gears, which drives the sample up the discharge line. Constructed of stainless steel 304, Teflon, and Viton®.*

Bladder pump *- Flexible bladder within. Device has check valves at each end. Gas from ground surface is cycled between bladder and sampler wall, forcing sample to enter bladder and then be driven up the discharge line. Gas does not contact sample. Materials may include stainless steel 316, Teflon, Viton, polyvinyl chloride (PVC), Silicone, Neoprene®, polycarbonate, Delrin®.*

Helical-rotor pump *- Water sample is forced up discharge line by electrically driven rotor-stator assembly. Materials may include stainless steel 304, ethylene propylene rubber (EPDM), Teflon, Viton, polypropylene.*

Gas-drive piston pump *- Piston is driven up and down by gas pressure controlled from the surface. Gas does not contact sample. Materials may include stainless steel 304, Teflon, Delrin, polypropylene, Viton, acrylic, polyethylene.*

Centrifugal pump *- Electrically driven rotating impeller accelerates water within the pump body, building up pressure and forcing the sample up discharge line. Commonly constructed of stainless steel, rubber, and brass.*

Peristaltic pump *- Self priming vacuum pump is operated at ground surface and is attached to tubing, which is lowered to the desired sampling depth. Sample contacts vacuum. Materials may include Tygon®, silicone, Viton, Neoprene®, rubber, Teflon.*

Gas-lift devices *- Gas emitted from gas line at desired depth forces sample to surface through sampling installation. Another method utilizes gas to reduce effective specific gravity of water, causing it to rise. Wide variety of materials available for tubing.*

Gas-drive devices *- Positive gas pressure applied to water within device's sample chamber forces sample to surface. Materials may include polyethylene, brass, nylon, aluminium oxide, PVC, polypropylene.*

Pneumatic *-In situ devices generally utilize the same operating principles as syringe samplers: a pressurized or evacuated sample container is lowered to the sampling port and opened, allowing the sample to enter. Materials may include PVC, stainless steel, polypropylene, Teflon.*

This chart outlines some of the general types of groundwater sampling devices available for hazardous waste site investigations. Most of the devices included are designed for use in existing monitoring wells installed in unconsolidated deposits. Special conditions such as fractured rocs or multilevel aquifers may call for in situ sampling devices as outlined in matrix. Suitability is based on currently available literature and is subject to change.

						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	*	*	*	*	*	*		*				*	*	*

Sampling devices on this chart are divided into two categories: (1) portable devices for sampling existing monitoring wells; and (2) in situ monitoring devices (often multilevel) that are permanently installed. Sampling devices construction materials (including tubing, haul lines, etc) should be evaluated for suitability in analysing specific groundwater determinands. It is assumed on this chart that existing monitoring wells are properly installed and constructed of materials suitable for detection of the determinands on interest. See references for additional information.

Sampling delivery rates and volumes are average ranges based on typical field conditions. Actual delivery rates are a function of diameter of monitoring installation, size and capacity of sampling device, hydrogeologic conditions, and depth to sampling point. For all devices rates should be carefully controlled to prevent aeration or degassing of the sample.

* Indicates device is generally suitable for application (assuming device is cleaned and operated properly and is constructed of suitable materials).

11.2 SOME ADDITIONAL COMMENTS AND NOTES

Bladder pump - As can be seen from the matrix table the bladder pump is suitable for sampling for all determinands. The bladder pump has the advantage over the helical rotor which is the only other all-rounder (almost, excepting for sampling coliform bacteria) in that the bladder pump is easy to disassemble in the field for cleaning and repair. The bladder pump is also relatively inexpensive. The pump alone costs about €400. The complete set-up which includes a surface pulse controller, the pump and all air-lines costs about €1000. The cost of the air supply is not included. This could be an air compressor, a set of SCUBA bottles or nitrogen gas bottles.

Point source bailer - From the table this device appears to be suitable for most components. However, the major drawback is that it cannot be used to purge the well. Using a bailer, there is a high probability that stagnant water will be collected. Also when collecting the sample there is a high probability that material such as iron hydroxide may be mechanically dislodged from the borehole or borehole casing wall, which may interfere with the results if precautionary measures are not taken. In general bailers should never be used for groundwater sampling. The main and very useful occasion for using a bailer is when collected LNAPLS. In particular, using a clear sided bailer enables one to visually see approximately how thick the layer of LNAPS is.

11.3 LOW-FLOW SAMPLING

When sampling high permeability aquifers, usually for water supply or hydrogeochemistry purposes, sampling mostly takes place at fairly high flow rates. Sampling at groundwater pollution sites however, often has to take place in low permeability formations. Using a normal sampling pump will often, if not always, rapidly lower the water level, often to the pump intake. This in turn induces much higher than natural rates of flow in the formation, mobilisation of formation particles, increased turbidity of sample, and thus biased results. Low-flow sampling is the technique that has developed in response to these problems. This involves using a pump that delivers 0.1 to 0.5 L/minute. The theory is that the pump is inserted opposite the screen or fracture, pumps at a low rate that does not disturb the aquifer material, thus keeping turbidity low, induces laminar flow that does not cause mixing inside the borehole, and thus enables collection of a representative groundwater sample. The method has been widely adopted for use in the USA where it is recommended or prescribed by US EPA. As a consequence there are a variety of commercially available pumping systems satisfying this method, and these are actively being promoted by the sales staff. The pumps can be peristaltic, bladder, electric submersible, or gas-driven. The most widely available are bladder pumps. Peristaltic pumps must not be used for volatile organics. An important aspect is that inserting pumps for a sampling causes mixing in the column, and thus requires an

extended purging time. Dedicated pumps left in the well are therefore preferred over any other system.

If you are designing a sampling program for a big issue pollution site and are considering low-flow sampling then you must do considerable additional reading. The influential paper strongly promoting the method by Puls and Barcelona (1996) is a must-read, while Stone (1997) discusses the pro's and con's. Many other documents, especially from the US EPA can be found by Googling.

WARNING 1

Make sure that a zone of high permeability on the outside of the casing, caused by a poorly designed gravel pack or damaged formation, does not allow vertical flow and short-circuiting. Doing low-flow sampling in such a borehole will be fruitless and misleading.

WARNING 2

The pumped water flows slowly delivery pipe, and thus will be affected by variable outside temperatures. Thus collecting a groundwater temperature during low-flow sampling is likely to be misleading.

11.4 Foot valve samplers

Foot valve samplers go under various names such as inertial foot-valve samplers and tubing check-valve samplers. These are non-return valves or foot-valves fitted to the end of reasonably stiff tubing. Rapid up and down movement of the tubing, making use of the inertia of the water column, results in water being pumped. These have been quite widely promoted as they are inexpensive, and can be left in-situ, thus reducing potential cross-contamination when sampling at a pollution site. Foot valve samplers would have been the answer to keeping sampling costs low, but they have a few drawbacks; the rapid physical up and down movement in the borehole loosens deposits from the sidewall; similarly aquifer material is loosened; if the borehole has a large well volume, you need to have a few very fit operators to ensure proper purging; and, operator variability reduces the repeatability of sampling procedure.

These foot valve samplers are useful for purging and cleaning newly drilled sampling wells and are recommended for this purpose. They are not recommended for sampling programs.

11.5 REFERENCES

Pohlman, K.F. and J.W. Hess 1988. Generalized ground water sampling device matrix. Ground Water Monitoring Review 8(4), 82-84.

Puls, R.W. and M.J. Barcelona. 1996. Low-flow (minimal drawdown) groundwater sampling procedures. U.S. Environmental Protection Agency, Groundwater issues report EPA/540/s-95/504. URL: http://www.epa.gov/ahaazvuc/download/issue/lwflw2a.pdf (last accessed on 5 November 2006)

Stone W.J. 1997. Low-flow groundwater sampling – Is it a cure-all? Groundwater Monitoring Review 17(2), 70-72.

CHAPTER 12

NEWLY DRILLED BOREHOLES

12.1 TURBID WATER AND CHEMISTRY

Turbid water is the enemy of proper groundwater sampling. If a turbid water-sample is acidified, then levels of metals will be overestimated. Filtration is a method of rectifying the problem, except that filtration can introduce other errors, such as removal of potentially mobile particles such as colloids. It is far better to be able to collect a water-sample that is not turbid, thus avoiding the need to fix the problem of turbid water. Thus, after drilling a new borehole, make sure that it is thoroughly cleaned before the contractor is allowed off site, or make sure that a borehole cleaning program is in place and has been completed before you arrive to collect groundwater samples for analysis.

Newly drilled boreholes also affect the groundwater chemistry as the fresh surfaces of rock are exposed to water. This must be reduced to a minimum by ensuring that all particles of rock are removed from the borehole by adequate cleaning of the borehole.

The drilling fluids that are used to maximize drilling efficiency have a much bigger than appreciated effect on the natural geochemistry of the groundwater. Drilling fluids contain a number of contaminants; including, sodium, sulphate, and carbon. Also drilling fluid may dilute the natural geochemical makeup; including, chloride, fluoride, and silicon. The most dramatic changes are seen with the carbon isotopes, ^{13}C and ^{14}C. Graham and Johnson (1991) calculated that when developing a newly drilled borehole at least 100 times the drilling fluid loss has to be removed before one can obtain reasonable hydrochemically representative samples. For the carbon isotopes, the volumes needed to be removed are even more.

So, the rule is “develop, develop and then develop the new borehole a little bit more”

12.2 MICROBIOLOGY AND NEW BOREHOLES

Most water borehole drilling fluids for rotary drilling are organic based (usually guar bean based). These result in high COD levels for months (GWMR Forum 1987), and up to a year, after completion. This high COD environment is a wonderful breeding ground for bacteria. The levels of HPC, *E. coli* and total coliforms increase rapidly soon after drilling and then slowly the numbers reduce. This occurs even with extensive purging and sterilization, so be warned that if the water is to be used for drinking water-supply, closely monitor the bacterial levels, and ensure the water is chlorinated before use. Regard any microbiological monitoring program results with

due care, understanding that the first year of monitoring data is probably not representative of the natural conditions.

12.3 REFERENCES

Graham, D.L. and Johnson, V.G. 1991. Effects of fluid rotary drilling on hydrochemical sampling results from deep boreholes in fractured Colombia River Basalt. J Hydrol 128, 171-212.

GWMR Forum 1987. How drilling fluids and grouting materials affect the integrity of groundwater samples from monitoring wells, Groundwater Monitoring Review 7(1), 33-38.

CHAPTER 13

PURGING THE BOREHOLE

13.1 INTRODUCTION

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 is modified by a number of processes:

- 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.
- Depletion of heavy metal species precipitated by sulphide (produced by the action of sulphate reducing bacteria commonly found in the stored water).
- Addition of foreign materials through the top of the borehole.

Purging of the borehole in practice 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 is sufficient and a safe working procedure. The usual order of stabilization is pH, temp, and EC, which stabilize 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 stabilization 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.

Open hole constructed boreholes can give results that can be erroneously interpreted, even when purging has been diligently carried out. This will apply when there is pressure gradient between the various horizons intersected, and vertical flow and short circuiting occurs. This is discussed extensively in Section 16.3 *Limitations of open borehole construction.*

13.2 FIELD PROCEDURE

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 intersection. 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.

(1) Measure the water level (see chapter 10).
(2) Measure the borehole depth.
(3) Then height of water column = borehole depth - depth to water level.
(4) Calculate the standing volume of water in litres by substituting in the formula:

$$V = \pi \times d^2 \times h / 4000$$

where V = Volume of standing water in litres
d = diameter of borehole in mm
h = Height of water column in metres

or from the information in table 13.1

(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 13.3). 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.
(7) Start pumping.
(8) Measure pumping rate in L/sec.
(9) Using the calculated well volume of step 4, calculate the pumping time needed to remove three volumes.
(10) Take continuous readings of pH, temp, EC and either Eh or DO.
(11) If the field chemistry stabilizes before three volumes are pumped, use the time for three volumes as the purge time at that pumping rate.
(12) If the field parameters have not stabilized (this is uncommon), continue pumping until they stabilize. This will be the purge time at that pumping rate.
(13) Record all the above for the Monitoring Programme Guide (Chapter 7) so that succeeding sampling runs can follow this established routine. Note that subsequent sampling runs should not measure the depth of the borehole described in step 2. By measuring the depth you tend to disturb material settled in the sump, and this will add to the turbidity. Seeing as the purging volume has been established and recorded in the Monitoring Programme Guide, the depth should only be checked once sampling of the borehole is complete.
(14) Once the borehole has been purged, with the pump still pumping, 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 (Figure 13.1).

(15) Collect the required groundwater samples.

(16) 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.

(17) Measure the borehole depth to check that collapse has not occurred since the previous sampling run.

Table 13.1 Borehole volumes per metre depth for different borehole diameters

Borehole diameter (inches)	Borehole diameter (mm)	Volume per metre depth (litre)
1	25	0.51
2	51	2.0
3	76	4.6
4	102	8.1
5	127	13
6	152	18
7	178	25
8	203	32
9	229	41
10	254	51
11	279	61
12	305	73

Please remove non-standard diameters from the table

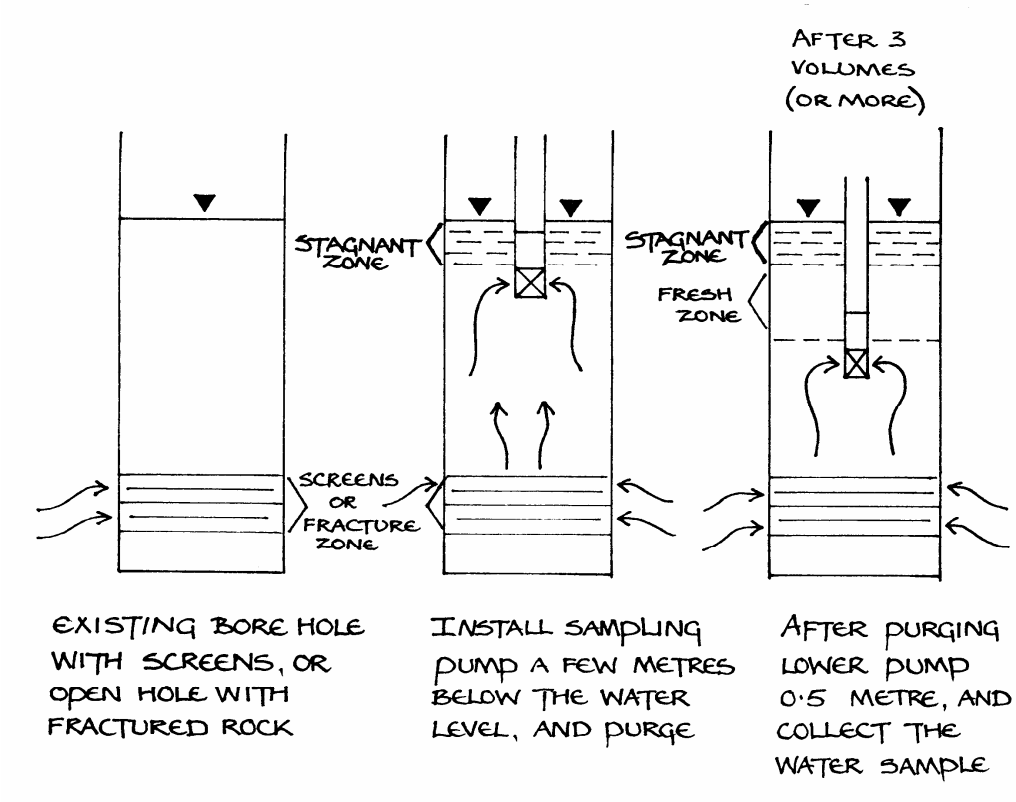

Figure 13.1 Sketch showing the method of positioning the sampling pump in a borehole in order to avoid contaminating the water sample with stagnant water (after Robin and Gilham 1987).

13.3 LOW YIELDING BOREHOLES

Some boreholes that are to be sampled may be low yielding and run dry when they are purged using the above normal pumping rates. If one is surveying an area for general aquifer hydrogeochemistry, leave the borehole to recover for a few hours. When returning, obtain as many measurements as possible for the water that is there, as this is representative groundwater for stable ionic species, but not for parameters susceptible to oxidation. If the objective is to assess hydrogeochemical processes or groundwater contamination issues, then consider using low-flow sampling techniques (Chapter 11.3). Low yielding boreholes pumped at high rates will give erroneous results for parameters that are affected by exposure to air.

13.4 TURBID WATER

Turbid water is the enemy of proper groundwater sampling (Chapter 12). If the borehole water becomes turbid or silty, the borehole must be re-developed before the next sampling run. Previously clear water turning turbid is usually caused by purging or sampling at a too rapid a pumping rate, and causing turbulence in the aquifer. Reduce the pumping rate to see whether turbidity reduces. Record the revised pumping rate in the Monitoring Programme Guide.

13.5 PURGING EQUIPMENT

Submersible and bladder pumps are suitable (Chapter 11). Bailers, 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.

13.6 TO PURGE OR NOT TO PURGE: THE DEBATE

When dealing with an aquifer with a reasonable permeability there should be no debate as to whether or not to purge. The two possible reasons why a groundwater quality investigator promotes the idea that a borehole in such an aquifer should not be purged are:

1. She/he does not possess the equipment to sample groundwater properly. Often the standard and only sampling equipment of these operators is a bailer, and
2. She/he is unwilling or too lazy to purge and sample the well properly.

Low-flow sampling (also called micro-purging) is a method that is widely used at contamination sites where the permeability of the aquifers is low to very low. At the outset it must be clearly understood that low-flow sampling **does not** equate to not purging. Low-flow sampling has evolved as a method of overcoming the problem of creating turbidity in low permeability formations when sampling using standard equipment. The low-flow pump (0.1 to 0.5 L/min) is positioned opposite the well-screen or fracture, and **then purging takes place** at these very low pumping rates. The theory of practice 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. Puls and Barcelona (1996) describe the purging and sampling procedure in detail, so if you have a contamination site with low permeability horizons, ensure you read this document.

Occasions when purging should not be done are:

- 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 bottom entry 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. Note that neither of these two procedures gives a measurement of the degree of contamination, but only gives a “yes, contamination is present”, or, a “no contamination does not appear to be present” answer.
- When you are about to conduct down-hole logging (Chapter 5) do this first and then purge the borehole for sampling.

13.7 REFERENCES

Puls, R.W. and M.J. Barcelona. 1996. Low-flow (minimal drawdown) groundwater sampling procedures. U.S. Environmental Protection Agency, Groundwater issues report EPA/540/s-95/504. URL: http://www.epa.gov/ahaazvuc/download/issue/lwflw2a.pdf (last accessed on 5 November 2006)

Robin, M.J.L. and R.W. Gillham 1987. Field evaluation of well purging procedures. Ground Water Monitoring Review 7(4), 85-93.

CHAPTER 14

FILTERING DEVICES

14.1 INTRODUCTION

Groundwater samples brought to the surface will, to varying degrees, contain dissolved species, colloids and suspended particles. One of the aims of low-flow sampling is to reduce (but seldom eliminate) the amount of larger 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). Suspended particles are still 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 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 program influences the contents of the Monitoring Program Guide which, in turn, prescribes the sampling procedures.

The pH and Eh of *in situ* groundwater is usually different to that same water at surface, and this is controlled by the levels of CO_2 (usually higher in the subsurface) and O_2 (usually depleted in the subsurface). The pH and Eh in turn control the solubility of metals, including iron and manganese. All hydrogeologists will, sooner or later, encounter the clear water sample that a few minutes, hours, or days later has an orange-brown floc. Some will have seen a water-supply borehole that, when switched on, spews out a gush of orange-brown ferric hydrous oxide precipitate. This slowly decreases until a few minutes, or tens of minutes later the water is clear. These are the result of CO_2 coming out of solution (and pH rising), and O_2 dissolving (and Eh rising), the iron oxidising from the soluble Fe^{+2} to the insoluble Fe^{+3}, which precipitates. When this happens calcium and other metal ions can co-precipitate, and other ions can also decrease by adsorption, or cation and anion exchange. These can include phosphate, molybdate, silicate, sulphate, borate, copper, lead, zinc and calcium (Braids et al*.,* 1987). When iron is present in groundwater it is very important to filter as rapidly as possible to prevent contact with air. If a sample with iron floc arrives at the laboratory what are they to analyse? Decant and analyse the supernatant, filter and analyse the filtrate, or acidify and analyse the resultant clear solution? Either of these will give an untrustworthy result. Rather filter immediately on-site and either acidify, or instruct the laboratory to acidify before analysis.

With boreholes drilled into low permeability aquifers, mostly at pollution monitoring sites, the problem is often turbid water. Thus the rate of pumping exceeds the rate of capacity of the aquifer to yield water, drawdowns are excessive, and turbulent flow

close to the borehole mobilizes formation material. Low-flow sampling (Chapter 11) is an approach to resolve the issue and obtain low turbidity water. Alternatively filtration should be applied. Burger (in Braids et al., 1987), presented three case studies where filtered and unfiltered samples had been collected and analysed. For all three sites the dissolved concentrations (filtered samples) of chemical analytes were significantly lower than the total concentrations (unfiltered samples).

Sometimes turbid water is a result of poorly constructed or inadequately developed boreholes. When these are encountered, the proper solution is to replace or rehabilitate the borehole. Filtering the water sample from such a well is poor practice, i.e. trying to fix a problem that should not be there.

The paper by Saar (1997) provides a good overview of filtration of groundwater samples. Braids et al. (1987) and Puls and Barcelona (1996) should also be read.

14.2 SAMPLING WATER SUPPLY BOREHOLES

Two decades ago sampling was mostly done to determine water quality fitness for consumption. Most of these boreholes and wells were completed in high yielding aquifers, and were pumped at reasonably high rates. The debate as to whether or not to filter was that these boreholes usually had a low turbidity, and that water from these boreholes was often consumed directly. Also, filtering added an additional variable that could alter chemistry. This last argument is essentially not applicable as proper field filtering procedures (as described below) virtually eliminates this effect. As to the first two arguments, if you suspect there may be a problem with the as-delivered water, then the proper approach is to collect both a filtered sample and an unfiltered sample. Have both analysed, and if the filtered sample is okay for consumption, but the unfiltered is not acceptable, then call in the water treatment experts to install an in-line treatment facility to remove the offending suspended particles.

14.3 FILTER APPARATUS

There are two methods of filtering, namely vacuum and pressure filtering. Vacuum filtering speeds up all the chemical changes that require one to filter a sample in the first place. Vacuum filtering is not recommended and will not be discussed here. Pressure filter devices are either in-line filters or syringe type filters.

An in-line filter is one which is connected to the pump discharge line. The advantage of this system is that the groundwater is filtered before coming into contact with oxygen and this is recommended. There are two types; a disposable in-line filter, or one which disassembles and takes a normal filter paper that is replaced after each filtering event. The advantage of the disposable version is that it is simple to use, it is

available either standard size for normal groundwater or as high capacity for large volumes or highly turbid samples; the disadvantage is that they are more expensive.

The hand held syringe system can be either a normal syringe or a syringe with a two way valve and a double piston cylinder. The normal syringe type is used for low turbidity waters. For more turbid waters additional pressure of the pump type is needed. Water is drawn into the large cylinder by pulling out the plunger. The valve is then turned to divert the water to the filter holder. Then a pressure is created to force the water through the filter by pumping the pressure piston. This device is acceptable for collecting filtered samples as, although the water sample is exposed to oxygen, the time span of less than 1 minute to filter the sample should cause no discernible bias.

14.4 FILTER MATERIALS AND SIZES

Filter membranes come in a variety of diameters, the common sizes being 47 mm, 90 mm, 102 mm and 142 mm. The 47 mm size is the most common. If the water has abundant suspended sediment, using the larger diameter filter means a slower rate of clogging and thus faster rate of filtering.

Taking into account the first paragraph of this chapter, and accepting that filtering will always be considered, the question is “what filter size should I use?” Filters come in a variety of pore sizes, ranging from 0.1 µm to 5 µm. The industry standard size recommended is 0.45 µm, but this allows smaller colloids to pass through.

If you want to understand the dissolved phase only, then use a 0.1 µm filter. At this pore size even bacteria will be removed. This filter size usually clogs very quickly making it worthwhile to use a large diameter filter and to check the required sample size carefully. If you do not have large diameter filters, then use a sandwich of filters, with a coarser (1 µm or 2 µm) filter first, then the finer filter.

If you want to understand the colloid phase, matters become more complex. Colloid composition and physical make-up vary considerably. Colloids range in size from 0.1 µm to 10 µm. Puls and Powell (1992) showed that colloids up to about 2 µm can move with groundwater, but larger colloids tend not to move. Colloids include large organic molecules such as humic and fulvic acids, aluminium oxides, iron hydroxides, manganese oxides and secondary clay minerals. They can have contaminants adhering to them and thus the smaller ones can increase the mobility of contaminants. Thus if the monitoring program requires an understanding of colloid transport, then add a second filtering program to ensure the colloid pollution load is included in the total contaminant loading.

For contaminant site monitoring, highly turbid samples must be avoided by firstly ensuring the boreholes are properly constructed, and secondly, adopting low-flow sampling techniques.

Filters are made from a variety of material such as cellulose nitrate, cellulose acetate, polycarbonate, glass fibre or PTFE (Teflon). For general purposes the first three are suitable for groundwater. If expecting a specific pollutant in very high concentrations consult a compatibility chart (e.g. Geotech).

14.5 GENERAL FIELD PROCEDURE

(1) When you are using a hand-held pressure filter device, first rinse it with deionized water.
(2) Insert the filter membrane correct side up, usually the side with the printed grid.
(3) Connect the in-line filter to the discharge pipe, or draw up a sample into the pressure-filter.
(4) Discard the first 50 mL.
(5) Collect the required amount of filtered sample.
(6) Discard filter membrane, 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 Monitoring Program Guide, and is adhered to for all sampling runs. This important!

14.6 REFERENCES

Braids O.C., Burger R.M. and Trela J.J. 1987. Should groundwater samples from monitoring wells be filtered before laboratory analysis? Groundwater Monitoring Review, Summer 1987, 58-67.

Puls, R.W. and Powell R.M. 1992. Transport of inorganic colloids through natural aquifer material: implications for contaminant transport. Envir Sci Techn 26(3), 614-621.

Puls, R.W. and M.J. Barcelona. 1996. Low-flow (minimal drawdown) groundwater sampling procedures. U.S. Environmental Protection Agency, Groundwater issues report EPA/540/s-95/504. http://www.epa.gov/ahaazvuc/download/issue/lwflw2a.pdf (last accessed on 5 November 2006)

Saar, R.A. 1997. Filtration of groundwater samples: a review of industry practice. Ground Water Monitoring Review 17(1), 56-62.

14.7 FILTER SUPPLIERS

The authors do not claim that the supplier's list is complete, nor can they guarantee the performance of the products

Geotech brochures, Geotech Environmental Equipment Inc. 1441 West 46th Avenue Unit 17, Denver, CO80211.

Millipore. http://www.millipore.com/catalogue.nsf/home (last accessed on 5 November 2006)

QED brochures. QED Groundwater Specialists, P.O Box 3726 Ann Arbor, MI148106.

Schleicher and Schuell Gmbh brochure, Postfach 4, D 3354 Dassel, Germany. Available in South Africa from Laboratory and Scientific Co (Pty) Ltd.

Whatman. http://www.whatman.com/ (last accessed on 5 November 2006)

CHAPTER 15

FLOW THROUGH CELL

15.1 THE FLOW THROUGH CELL

There are three factors that change when groundwater is removed from the aquifer and brought to the surface for analysis:

(1) the hydrostatic pressure certainly changes,
(2) the temperature may change,
(3) the sample comes in contact with the atmosphere.

There is not much the sampler can do to maintain pressure. Temperature can be controlled somewhat by pumping long enough so that the sampling equipment attains the groundwater temperature. Contact with the atmosphere can cause loss or gain of various dissolved gases and can be avoided by using well-designed flow-through cells. pH, Eh, DO are particularly sensitive to air contact and reliable measurements of these parameters require protection against air interaction.

A flow through cell is a closed container with groundwater flowing in at the bottom and out at the top in such a way that no air is trapped inside. pH, Eh and DO probes can be inserted into the flowing water through waterproof glands on one side of the container in order to take the field readings. Many designs of flow through cells exist (Walton-Day et al., 1990) and more can be found on the internet.

The recommended design (Figure 15.1) is that of Garske and Schock (1986). The advantages of this design are:

- Transparent sides so that the coating of electrodes with bubbles, colloidal material or mineral precipitates can be observed;
- A conical shape to minimise the trapping of air bubbles and to ensure laminar flow: provided the flow rate is low enough.
- The relatively large diameter which, if combined with a slow rate of through flow, reduces "stream potential", which might lead to erroneous pH readings.
- An arrangement of probes with respect to the water flow direction so that interaction between probes is avoided.

It is essential to maintain the water flow rate through the cell to less than 1 litre/minute to avoid turbulence and stream flow potential on the pH probe. Some form of valve system with a bypass line is essential to control the flow rate through the cell. This will aid in-line filtration and sampling after the field measured parameters have stabilized.

An alternative design (the Sheffield LFC cell) allows the water flow in series through separate small cells each containing one electrode (Waterra 2003). With this design

the sequence of probes is important since some probes (e.g. DO) can alter the water and a minimum flow rate needs to be maintained to minimize this alteration.

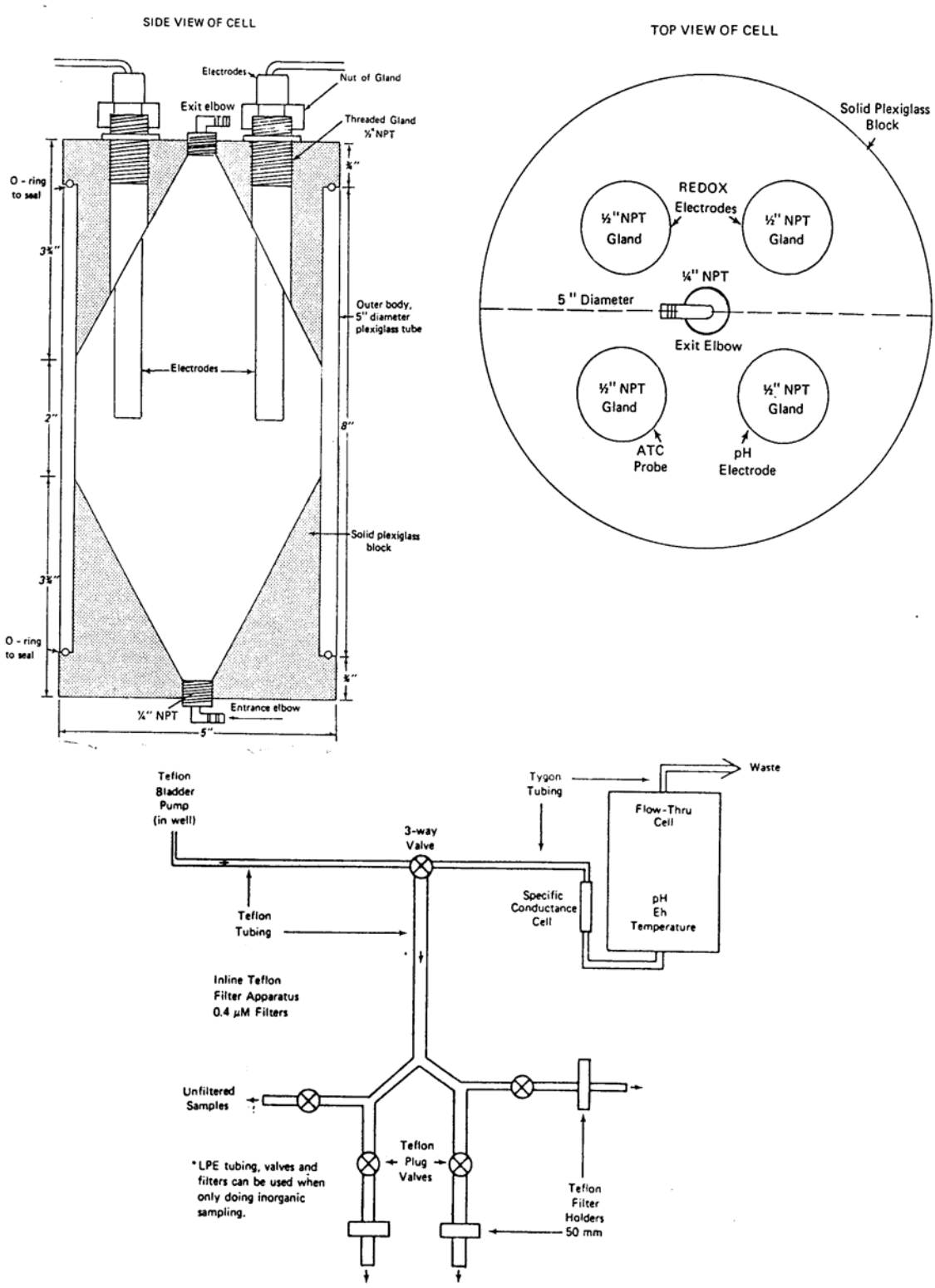

Figure 15.1. Diagrammatic views of the essential features of the flow through cell (Garske and Schock 1986).

15.2 THE BOTTLE AND CORK METHOD

An improvised cell has been made on occasion when measurements had to be taken and the right equipment was not available. While it should not be considered good practice, these types of short-cuts are occasionally necessary and can be quite effective provided they are used with caution.

The system requires a clear bottled water bottle, a rubber bung and the necessary tubing through the bung to control the flow rate of the water (Figure 15.2). Water is fed through the neck of the bottle to its bottom and led out through a short tube at the top. The probe is held in position in the bottle through the rubber bung. One could also use Prestik® provided the internal pressure of the system can handle it. It is essential to keep the water flow rate low and to ensure that all air bubbles are eliminated.

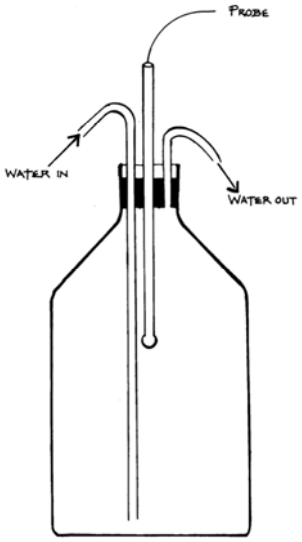

Figure 15.2. Sketch of improvised flow-through cell. The outlet tube should not protrude through the stopper into the bottle to ensure that all bubbles can readily be removed from the cell.

15.3 THE OPEN BUCKET METHOD

An even more primitive (but practical) solution is to feed the water to the bottom of a bucket and allow the bucket to overflow. The electrodes should then be suspended in the bucket in such a way that the sensors do not touch the bottom, yet are deep enough in the water for atmospheric air not to have an influence.

15.4 REFERENCES

Garske E.E. and M.R. Schück 1986. An inexpensive flow through cell and measurement system for monitoring selected chemical parameters in groundwater. Groundwater Monitoring Review 6(3), 79-84.

Walton-Day, K., D.L. Macalaudy, M.H. Brooks, and V.T. Tate 1990. Field measurement of ground water redox chemical parameters. Groundwater Monitoring Review Fall 1990.

Waterra 2003. The Sheffield LFC flow-through cell. URL: http://www.waterrauk.com/pages/SamplingAccessories.asp#Flow-Through%20Cell (last accessed on 5 November 2006)

CHAPTER 16

MULTIPLE LEVEL SAMPLING

16.1 INTRODUCTION

In a study of natural groundwater chemistry or contamination, it is often important to obtain detailed information on the vertical distribution of the chemicals. In all geological materials there are heterogeneities and especially so for hydraulic conductivities. Figure 16.1 shows the effect of simple, layered heterogeneities on chemical transport patterns.

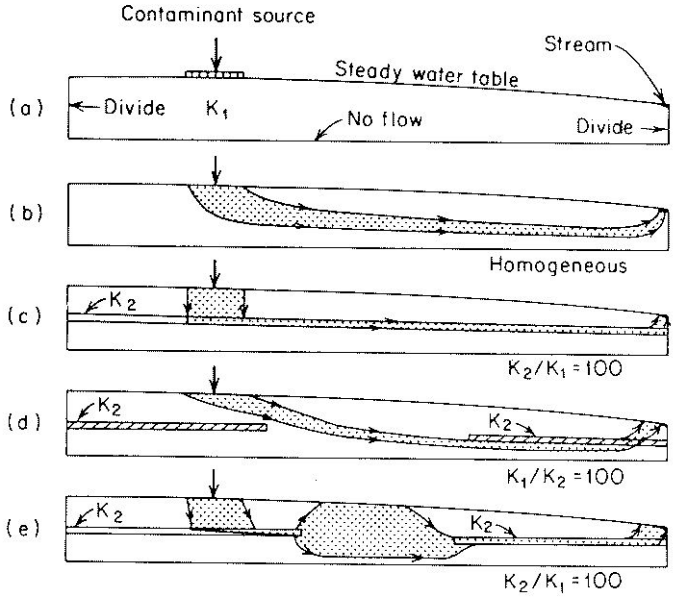

Figure 16.1 Effect of layers and lenses on flow paths in shallow steady-state groundwater flow systems. (a) Boundary conditions; (b) homogeneous case; (c) single higher-conductivity layer; (d) two lower-conductivity lenses; (e) two higher-conductivity lenses (Freeze and Cherry 1979, p. 397)

Level-determined samples, collected from known depth intervals in an aquifer are becoming increasingly important in hydrogeological studies. They are valuable for studies where the focus is on detailed chemical transport processes or three dimensional characterisation of pollution for design and evaluation of remediation systems (Lerner and Teutsch 1995).

16.2 METHODS OF CONSTRUCTION AND APPROACHES FOR MULTILEVEL SAMPLING

Multilevel sampling installations are grouped into three methods of construction:

(1) Multiple monitoring boreholes at one site.
(2) Single monitoring borehole with multiple screens and piezometers installed.
(3) Single monitoring borehole with a single long screen ("flow-through" or “open-hole”).

The description of sampling systems in this document is by no means exhaustive, but covers a wide range of methods reported in the literature over the last few decades. Although becoming more common in routine pollution investigations, multilevel sampling is a specialised groundwater sampling activity and the approach taken is often designed or adapted to meet the specific requirements of a particular project or site. The chapter on down-hole logging (chapter 5) and the section on low-flow sampling (chapter 11.3) should also be referred to. Some of the more common multi-level sampling approaches are illustrated in Fig 16.2.

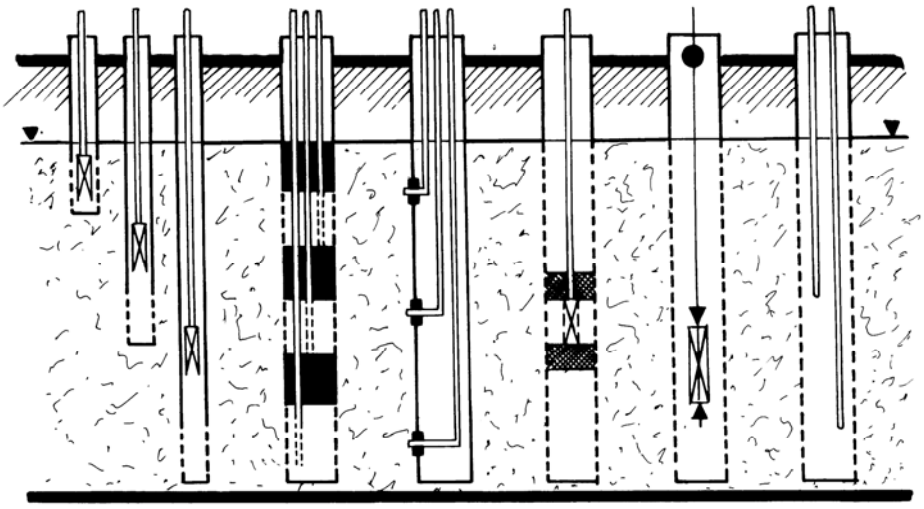

Figure 16.2 Types of monitoring boreholes and sampling devices (After UNESCO 1972)

Version A This is a group of monitoring boreholes at the same site. Each borehole has a short length of screen at different depths. This method is the safest way to ensure that cross contamination does not occur, but is also the most expensive.

The critical aspect of construction is that the annulus along the outside of the borehole casing must be carefully constructed to ensure that short-circuiting does not take place along the space between the outside of the casing and the aquifer material. Thus in borehole A3 (the deeper of the 3) the screens are set at the bottom of the borehole. On the outside, opposite the screens, must be installed the filter-pack. Above the filter pack, on the outside, must be installed a seal (usually of benthonite) that will prevent water from the upper horizons travelling down the annulus and producing incorrect answers for the sample collected.

Version B This method consists of multiple piezometers installed at different depths in a single borehole. Each zone is sealed off from the adjacent zone using either a benthonite or a grout seal. The critical aspect of this construction method is the integrity of the seal. If a complete seal is not obtained, vertical flow will be induced during sampling. If the piezometric level is less than 8 metres from surface, suction lift can be used to collect samples (but is not suitable for gases and VOCs). If greater than 8 metres then the piezometers will have to be 50 mm to 65 mm outer diameter in order to accept a down-the-hole pump, or 25 mm to accept a 19 mm bladder pump.

The number of piezometers that can be installed in a borehole with a water level deeper than 8 metres is thus dependent on the diameter of the drilled borehole and the practicalities of properly introducing the seal. A 160 mm borehole will take two, at most three piezometers and a 200 mm borehole will take three to four piezometers.

Version C This method consists of a single casing fitted with openings (ports) at different levels. These are very useful in aquifers where the water-table is at most 8 metres below surface as the samples can then be collected by suction-lift. Suction-lift is not a suitable sampling method for gases and VOCs. The usual construction is to use 3 mm silicone tubing to the sampling port. If, however, you wish to obtain water-levels, at least 20 mm tubing should be used so that the water level gauge can be inserted into each piezometer tube. The “multi-port sock sampler” of Schirmer et al. (1995), Jones and Lerner (1995), described later in this chapter is such an example.

Versions D, E and F These methods are described here as they may be encountered in literature or the field. None of versions D, E or F are recommended for collection of groundwater samples from multi-layered or multi-fractured aquifers. They are not recommended as short-circuiting is quite likely to occur in such boreholes. Later in this chapter this theme is expanded upon. The borehole is completed with one long screen for unconsolidated material or is open-hole construction for hard-rock. For Version D; an inflatable double packer system is moved to various positions and a sample is pumped from between the packers. For Version E; the depth-specific grab sampler, usually a Kemmerer sampler or syringe device, is lowered to the required depth and a sample collected. For Version F; two or more pumps are used to simultaneously collect samples from different depths.

16.2.1 Single-hole multilevel sampling

Multiple boreholes at one sampling point (Version A) and multi-level piezometers systems (Version B) are expensive to construct. Thus several approaches to modifying the single-hole construction have been developed.

- Packer systems
- Multi-port sock samplers

Packer systems

Packer systems are used to isolate a specific zone in an open borehole for sampling. The system involves lowering one of more inflatable packers to a desired depth in a borehole and then inflating the packers to seal off the flow of water at that depth. The common configuration is either, a double packer system with packers above and below a narrow pumped zone, or, a single packer separating an upper and a lower zone of the aquifer, or separating two fractures.

This method must be used with caution. The borehole creates a path of very high hydraulic conductivity. Thus if there is the slightest hydraulic pressure gradient between two horizons, the horizon with the higher of the hydraulic gradients will flow in the borehole and into the horizon with the lower pressure. Collecting samples using temporary moveable packers will result in a correct sample for the one horizon, but a mixed sample for the other horizon. The correct method is to leave a permanent packer in the borehole, and only collect the samples after the borehole has stabilised.

Multi-port sock samplers

A sock sampler consists of one or more elongated packer balloons or “socks” (up to several tens of metres in length) which are inflated with air or water after installation in the borehole (Schirmer et al*.,* 1995, Jones and Lerner 1995). This displaces the water over a long section of the borehole and avoids vertical circulation. Multiple sampling ports are created by tubing that runs down from the surface either inside the packer elements or between the packer and the borehole casing. Multi-port sock samplers may be used as removable devices or as semi-permanent installations up to a maximum depth of around 100 metres.

Several modifications have been made to the multi-port sock samplers since the original concept was proposed by Andersen (1982). Jones et al. (1999) describe a double-walled sock sampler filled with benthonite slurry. Inlet ports at fixed depth intervals along the sock are connected by Teflon tubes to individual gas drive or bladder pumps inside the sock. Each pump is sampled via an HDPE tube running to the surface. The pumps are not required if the water table is less than 9 metres below surface, as the samples can then be retrieved by suction (not if sampling for volatiles).

16.2.2 Open-hole multilevel sampling systems

Purpose constructed boreholes (Versions A, B & C above) are expected to give the best confidence in the results (Gillham et al., 1983), but it is expensive to construct dedicated multilevel boreholes. Several approaches have therefore been developed for multilevel sampling in open boreholes which are used for other purposes. None of these are recommended for long-term monitoring. These are only to be used if the boreholes are used for other purposes, and one wishes to gain an indication of sub-surface conditions. See Section 16.3 below.

Examples of open hole multilevel sampling systems include:

- Packer systems
- Bundled piezometer systems
- Diffusive gel/dialysis membrane samplers
- Depth specific samplers
- Separation pumping
- Baffle systems

Bundled piezometer systems

Bundled piezometers are similar in design to the multiple piezometer system shown in Figure 16.2 Version B. Essentially the system consists of a number of narrow tubes installed to different depths in an open borehole. The tubes may be bundled together (e.g. Powell and Puls 1993) or strapped to the outside of a rigid support casing (e.g. Taylor et al., 2000). Holes may be punched in the bottom few centimetres of each tube to increase the intake area. The samplers require some time to equilibrate after installation (usually several days, depending on the aquifer flow properties) and are then sampled from the surface by a peristaltic pump or inertial hand pump. When pumped at very low rates, the bundled piezometer allows a large number of samples to be collected at relatively small depth intervals.

The bundled piezometer system can be installed as a removable sampler in fully screened boreholes or uncased hard rock boreholes. It can also be installed as a permanent multilevel sampling system by inserting a casing-supported bundle in an uncased auger hole in unconsolidated sediments. In uncased boreholes, it is necessary to sheath the intake area with a mesh or gauze “sock” fitted over the end of each the tube. The size of the mesh should be chosen to prevent the aquifer sediments from entering the tube.

This method must be viewed with due caution. The problem of vertical flow in the borehole and resultant ambiguous results for hydrogeochemistry is not resolved with this method.

Diffusive gradient gel/dialysis membrane samplers

These samplers work on the principle of diffusion or dialysis to accumulate dissolved species for chemical analysis. No pumping is required. Several diffusive gel units or

dialysis units may be installed at the desired sampling depths, e.g. by suspension on a length of weighted fishing line or mounting at desired intervals in a rigid sampler inserted into an open borehole. The sampler is left for a period of time to allow the units to equilibrate with the dissolved species in the groundwater and then recovered for analysis of the accumulated solutes in each unit. The accumulated concentrations of solutes in the dialysis cell or gel can be related back to the original concentrations in the groundwater at that depth.

The dialysis cell sampler is suitable for obtaining undisturbed groundwater samples over small vertical intervals. Ronen et al. (1986) used a dialysis cell sampler to measure multilevel electrical conductivity and major anion concentrations (chloride, nitrate, sulphate) at 3 cm intervals just below the water table in an open borehole. The dialysis cells mounted on a PVC rod were filled with distilled water and left in the borehole to equilibrate for 30 days before analysing the equilibrated solutions.

A diffusive gradient thin film (DGT) is a method involving a gel disc or strip in a suitable holder (Harper et al., 1997, Zhang and Davison 1999, DGT Research 2003). The gels are designed to accumulate specific dissolved species from sediment pore waters. Specific gels are available for sampling metals, phosphorus, sulphide or caesium. There are also open pore diffusive gels for more general application and restricted pore size gels for labile inorganic species. DGT samplers have been used in open water systems and may find future application in multilevel groundwater sampling.

This method must be viewed with due caution. The problem of vertical flow in the borehole and resultant ambiguous results for hydrogeochemistry is not resolved with this method.

Depth-specific samplers

These consist of a plastic or metal tube or vessel, sometimes evacuated or over-pressurised with an inert gas or air. The sampler is lowered by rope or cable to the desired depth and an inlet valve opened to allow the borehole water to enter the sampling vessel. The device is then recovered to the surface and the sample poured into a sampling bottle or delivered in the pressurised vessel to the laboratory. The trigger for the valve system is usually operated electromagnetically. One of the simplest and cheapest depth-specific samplers is an open top bailer with a bottom ball valve. When lowering the bailer, the valve is open and groundwater moves through the bailer. When the bailer is withdrawn, the valve closes during upward movement, trapping a sample of water from the maximum depth to which the device was lowered.

Although a common method of depth specific sampling, this method is not very accurate. This method is not recommended for proper sampling in multi-layered aquifers.

Separation pumping

This system uses three pumps: two “flow control” pumps are positioned one at the top and the other at the bottom of the borehole and one “sample pump” in the middle. When both flow control pumps are in operation, they separate the flow of water in the borehole into two components on either side of a “water divide”. A flow meter is used to locate the position of the water divide and the sample pump is positioned at this depth. Flow at the water divide is assumed to be horizontal i.e. pumping the sample pump at a very low rate (less than 1% of the total rate) allows a groundwater sample to be collected from the discrete depth in the aquifer where the water divide is located. The position of the water divide can be manipulated by changing the pumping rate of the flow control pumps to enable sampling of a vertical chemical profile. The method requires accurate prior knowledge of the aquifer transmissivity and specific capacity of the borehole and a high level of skill to operate. It is also limited by the diameter of the borehole which may not be wide enough to accommodate the three pumps (Nilsson et al., 1995a, b, Jones and Lerner 1995).

Baffle systems

Baffle systems consist of a packer with an open-ended inner tube of slightly smaller diameter than the borehole. The function of the baffle is to guide the flow above the packer. A purging pump is operated above the baffle element creating vertical flow inside the borehole through the baffle. Horizontal radial flow should develop around the borehole. This allows level determined samples to be collected just above the packer in the annulus between the baffle and the borehole screen. The sample pump must be pumped at a lower flow rate than the rate of inflow through the screen (Nilsson et al., 1995a, b, Jones and Lerner 1995).

16.2.3 Summary of multilevel sampling techniques

Table 16.1 has been adapted from Lerner and Teutsch (1995) to summarise the features of various multilevel sampling techniques.

Table 16.1. Features of multilevel groundwater sampling techniques (After Lerner and Teutsch, 1995, see text for details)

	Individual boreholes	Installed multilevel piezometers	Depth specific samplers	Packer systems	Separation pumping	Baffle systems	Multi-port sock samplers	Bundled multilevel piezometers	Gel/dialysis samplers
Environment									
Type of borehole	Dedicated	Dedicated	Open	Unscreened	Open	Open, no pack	Unscreened	Open	Open
Short-circuiting & mixing	None, if screens are short	None, if properly grouted	Occurs	None, once installed	None, if pumps run	Sometimes	No	Sometimes	None, no pumping
Investigation type	Monitoring or any other	Monitoring	Recon-naissance	All, but poor monitoring	All, but poor monitoring	All, but poor monitoring	All, poor for reconnaiss.	Monitoring or any other	Recon-naissance
Equipment									
Capital costs	Mod – high	Mod - high	Very low	Low	Low	Low	Moderate	Low	Moderate
Running costs	Low	Low	Very low	Moderate	Moderate	Moderate	Low	Low	Low
Ease of use	Simple	Simple, once installed	Very simple	Complex, need expert	Complex, need expert	Complex	Simple, once install.	Simple	Simple
Availability	Standard drilling	Specialised drilling	Commercial	Commercial/ home-built	Commercial pumps	No supplier, home-built	No supplier, home-built	No supplier, home-built	Commercial/ home-built
Decontamination	Needed if pumps moved	If using submersible pumps	Needed between boreholes	Difficult for packers	Needed for sample pump only	Needed for baffle & sample pump	Only between boreholes	Only between boreholes	Not needed, disposable components
Performance									
Level accurate	Yes, but inflexible	Yes, but inflexible	No	Yes, to a few metres	Yes, very flexible	Yes, very flexible	Yes	Yes, but may mix	Yes, fine resolution
Maximum depth	Deep	Deep	Deep	Deep	Deep	Deep	< 100 m	Shallow	Shallow
Volume sampled	Small – Mod	Small – Mod	0.5 – 2 L	Moderate	Large	Large	0.1 – 2 L	Small – Mod	Very small
Flushing ability	Good	Good	None	Good	Good	Good	None	Poor	None
Effect on sample	Variable	Variable	May degas	Degas/sorb	Degas/sorb	Degas/sorb	Degas/sorb	Degas/sorb	Variable
Multipurpose use of borehole	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes

16.3 LIMITATIONS OF OPEN BOREHOLE TECHNIQUES

Open borehole methods, whether in unconsolidated aquifers, or in hard-rock aquifers, or in fractured rock aquifers, carry the risk of obtaining poor or unrepresentative samples (Lerner and Teutsch 1995, Shapiro 2002). Gillham et al. (1983) seriously questioned the validity of the "flow-though assumption" using open boreholes, in view of the fact that the effective hydraulic conductivity inside the borehole is infinitely larger than the hydraulic conductivity of any formation. Any slight vertical hydraulic gradient in the aquifer around the borehole contributes to some degree of vertical movement (and thus mixing) inside the borehole. Open boreholes are known to act as a short circuit, allowing groundwater to flow from one aquifer layer to another. Shapiro (2002) examined the theory, conducted field experiments and concluded that "It is recommended that open boreholes be permanently outfitted with borehole packers, or borehole liners, in instance where maintaining the hydraulic and chemical stratification in the aquifer is of importance".

Gravel packs are also usually of high permeability relative to the aquifer formation and can provide a short circuit along the outside the borehole, even if flow is prevented in the borehole. This vital point is occasionally overlooked when designing the borehole construction. Make sure that the outside annulus between the casing and the undisturbed aquifer material is properly sealed, thus isolating upper from lower aquifer zones.

An investigation by Rödelsperger et al. (1989, Rödelsperger et al. (1989, 1991) provides proof of short circuiting in an unconsolidated aquifer with primary porosity. Nitrate (as NO_3) at 150 mg/L was found in a series of three shallow boreholes and a suction cup over a distance of about 200 m, perpendicular to the flow direction in an unconsolidated aquifer. However, in a shallow (6 m) borehole in between the contaminated boreholes, only 30 mg/L of nitrate was observed, rather than the 150 mg/L which was expected. This shallow borehole is adjacent to a deep (30 m) borehole, which allowed low nitrate groundwater to be displaced upwards from deeper in the aquifer. The deep borehole acted as a short circuit with respect to the various pressure heads in different depths.

Before the borehole was equipped with stationary packers, a large volume of up-flowing, low nitrate groundwater infiltrated the shallow aquifer. Even after a long purging period using a temporary double packer system, the original groundwater of the shallow aquifer was not intercepted. Subsequent to the first sampling run a permanent (also called stationary) packer system was installed in the deep borehole. This packer separated the lower from the upper aquifer. After allowing the system to stabilise, multilevel sampling took place and high levels of nitrate, as expected, were obtained in the shallow borehole, as well as in the upper zones of the deep borehole Rödelsperger et al. (1991).

Short-circuiting in boreholes allows water types to be transferred vertically in the aquifer, causing changes in groundwater quality in the region of the borehole where

hydraulic head is lower. The effect is more severe with stronger vertical gradients. As a result, there is potential ambiguity about the source of the water in multilevel sampling. Vertical gradients can also spread contaminants to regions that were previously uncontaminated. For a more detailed discussion on this phenomenon, see Lerner and Teutsch (1995).

Repeatability of the vertical profile of hydrochemical measurements from one sampling run to another also does not necessarily guarantee that the designed sampling method is accurate. This merely shows that the water is sampled in a consistent manner, rather than that the composition profile is undisturbed (Gillham et al., 1983).

16.4 FRACTURED ROCK CONSIDERATIONS

Boreholes drilled in secondary or hard-rock aquifers (also called basement or bedrock formations), are usually completed as open-hole construction. Occasionally collapsing ground will require slotted casing. Those boreholes with two or more water-strikes are likely to be "flow-through" boreholes, as described above. Thus the results of groundwater quality sampling conducted in these situations must be viewed with due caution. Shapiro (2002) provides a detailed discussion of the ambiguities involved in sampling boreholes intersecting multiple fractures. This article must be required reading for all hydrogeologists working in hard-rock terrains.

In the initial exploratory phase, "flow-through" boreholes can be sampled in order to gain an initial understanding of the aquifer. For detailed follow-up work, either multiple wells completed at different depths or multiple piezometers with grout/benthonite seals or semi-permanent packers must be used. Down-hole logging techniques (chapter 5), especially electrical conductivity and temperature logs, are a useful way of detecting the target zones for multilevel sampling in fractured rock boreholes during the exploratory phase.

16.5 CORE VOLUME SAMPLING

The sampling methods above can all be categorised as “flux samples” i.e. they are all captured from flowing water, whether by pumping, grab sampling or chemical equilibration, in a borehole drilled into the aquifer. An alternative approach is to obtain a “volume sample” by coring a volume of saturated or partly saturated aquifer material and then centrifuging or leaching out the liquid fraction.

Volume samples capture the volume of water within an aquifer volume irrespective of its mobility, while flux samples contain a mixture of flow streams in proportion to their velocities (or aquifer permeabilities) (Lerner and Teutsch 1995). A flux sample may have a different composition depending on the pumping rate, while the composition of a volume sample is fixed. Volume sampling is often used to obtain hydrochemical

profiles in low permeability formations e.g. clay aquitards or for pollution investigations where the total mass of contaminant must be established.

16.6 REFERENCES

Andersen, L.J. 1982. Techniques for groundwater sampling. Memoirs of the 17th Congress of the International Association of Hydrogeologists. Impact of agricultural activities on groundwater. Novinar, Prague, p115 – 124.

DGT Research 2003. Diffusive Gradient Thin film. URL: http://www.dgtresearch.com/ (last accessed 5 November 2006).

Freeze, R.A. and J.A. Cherry 1979. Groundwater, Prentice-Hall, New Jersey.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry 1983. Groundwater monitoring and sample bias. Department of Earth Sciences University of Waterloo, Waterloo, Ontario. Prepared for Environmental Affairs Department, American Petroleum Institute.

Harper, M., Davison, W. and Tych, W. 1997. Temporal, spatial and resolution constraints for in situ sampling devices using diffusional equilibration: dialysis and DET, Envir Sci Techn 31, 3110-3119.

Jones, I and Lerner, D.N. 1995. Level-determined sampling in an uncased borehole. J of Hydrol 171, 291 – 317.

Jones, I., D. N. Lerner and O. P. Baines. 1999. Multiple sock samplers: A low-cost technology for effective multilevel groundwater sampling. Groundwater Monitoring Review Winter 1999, 134-142.

Powell, R. M. and R. W. Puls 1993. Passive sampling of groundwater monitoring wells without purging: multilevel well chemistry and tracer disappearance. Journal of Contaminant Hydrology 12, 51-77.

Lerner, D. N and Teutsch, G. 1995. Recommendations for level determined sampling in wells. J of Hydrol 171, 355 – 377.

Nilsson, B., Jakobsen, R. and Andesen, L.J. 1995a. Development and testing of active groundwater samplers. J of Hydr 171, 223 – 238.

Nilsson, B., Luckner, L. and Schirmer, M. 1995b. Field trials of active and multiport sock samplers in gravel-packed wells. J of Hydrol 171, 259 – 289.

Rödelsperger, M., J. Kiefer and T. Ball 1989. Fallstudien über Stickstoffumsetzungen in Boden und Grundwasser in den Gebieten Bruchsal/Karlsdorf-Neuthard und Lobdengau. Final report of projects 75-84.02 and PW 86-038. DVGW- Forschungsstelle am Engler-Bunte-Institut, Univ Karlsruhe.

Rödelsperger, M.U., Rohmann and F. Frimmel 1991. A stationary packer system for layer-wise groundwater sampling in monitoring wells - technique and results. Wat. Sci. Tech. 23, 545-553.

Ronen, D., Magaritz, M and Levy, I. 1986. A multi-layer sampler for the study of detailed hydrochemical profiles in groundwater. Water Research 20, 311-315.

Schirmer, M., Jones, I., Teutsch, G. and Lerner, D.N. 1995. Development and testing of multiport sock samplers for groundwater. J of Hydrol 171, 239 – 257.

Shapiro, A.M. 2002. Cautions and suggestions for geochemical sampling in fractured rock. Groundwater Monitoring & Remediation, 22(3), 151 – 164.

Taylor, R.G., Barrett, M.H., Baines, O.P., Trowsdale, S.A., Lerner, D.N. and Thornton, S.F. 2000. Depth variations in aquifer hydrochemistry using a low-cost, multilevel piezometer. In Sililo et al. editors, Groundwater: Past achievements and future challenges, IAH2000 Conference Proceedings, Balkema, Rotterdam.

UNESCO 1972. Ground-water studies, UNESCO Press, Paris.

Walton-Day, K., D.L. Macalaudy, M.H. Brooks, and V.T. Tate 1990. Field measurement of ground water redox chemical parameters. Groundwater Monitoring Review Fall 1990.

Zhang, H. and Davison, W. 1999. Diffusional characteristics of hydrogels used in DGT and DET techniques. Anal. Chem. Acta 398, 329-340.

CHAPTER 17

PROTECTIVE CLOTHING

Protective clothing to protect the sampler may be required in some waste site investigations. The degree of protection required depends upon the nature of the site being sampled and the physical, chemical and biological properties of the water that will be handled. In many cases the individual waste products are relatively harmless but when combined in the waste disposal site, they can react to produce hazardous by products. All countries will have legislation that lays down stringent guidelines as to safety equipment that must be worn at any site where hazardous materials may be found.

To assess the nature of the hazard, a photo ionization meter or explosimeter can be used. Lower the probe down the well, take a reading, record, and then take appropriate action. This should be done on the pilot sampling run and potential hazards noted.

Waste disposal sites can be split into two classes, namely;

- Hazardous waste sites
- Non-hazardous waste sites

Hazardous waste sites are specially constructed containment sites for the disposal of waste that is regarded as hazardous. Such a site requires an impermeable membrane or a relative impermeable layer that will efficiently contain both the waste and the leachate in the site or in the immediate surroundings of the site.

Non-hazardous waste sites will be where household and other general waste such as building rubble can be disposed. Such a site will have been characterized to emit leachate very slowly and continuously. The leachate is regarded as relatively harmless in terms of toxic compounds, and will be located in a position that will not endanger an existing or future water resource.

If sampling groundwater at a hazardous waste site, it is essential to wear personal protection equipment (PPE). At other sites do not be surprised to find that the explosimeter indicates dangerous conditions and that PPE should be worn when collecting groundwater samples.

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 precautions. It is the responsibility of the Project Leader 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.

Some of the chemicals used on site and preservatives used to treat samples are themselves hazardous, such as mercury (from thermometers that may break), ZoBell’s solution, nitric acid and sulphuric acid. Due precaution must be taken when handling these materials.

CHAPTER 18

DECONTAMINATION

18.1 INTRODUCTION

Collecting groundwater quality samples is expensive in terms of both time and money. Obtaining erroneous results through cross contamination of boreholes is unforgivable. Following a few simple rules as set out in section 18.2 will significantly 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 determined by the monitoring programme and the results required. So it is up to you to determine what is needed, to write it up in the Monitoring Programme Guide (chapter 7), to ensure that the guidelines are adhered to and at intervals to carry out a performance audit (chapter 6) as part of the Q.A. programme.

18.2 BASIC DECONTAMINATION ROUTINE

Basic decontamination procedures apply to monitoring programmes where the credibility of the chemical data is not a critical aspect of the monitoring programme. This does not imply that the results obtained will not be correct, but rather that if the credibility of the chemical data must withstand legal scrutiny, this basic decontamination routine is not acceptable and the procedure as detailed in section 18.3 must be followed. When sampling for trace elements, especially trace organic compounds which are measured at parts per 10^{-9} or 10^{-12}, and also for trace metals, the basic procedure might be inadequate.

(1) Use sampling equipment that is easy to clean and pumps that can easily be disassembled.

(2) Start sampling at the borehole with the LOWEST concentration of chemicals and end up at the borehole with the HIGHEST concentration of chemicals.

(3) Purge the borehole correctly, i.e. follow the procedures of chapter 12. Following this procedure will ensure that the sample collected is not cross-contaminated. If there is some chemical carry over, only the stagnant water will be affected.

(4) Dispose of the purged water safely so that cross-contamination will not occur.

(5) After the last borehole has been sampled clean your sampling equipment as follows:

- Thoroughly rinse with phosphate free detergent solution;
- Rinse with tap water;

- Give final rinse with distilled water;
- Air dry.

18.3 DECONTAMINATION AT SENSITIVE SITES

Parker and Ranney (1997a, 1997b) carried out a series of investigations of the efficiency of various decontamination protocols. They tested stainless steel, polyvinyl chloride (PVC) and poly-tetra-fluoro-ethylene (PTFE or Teflon) for exposure to three VOCs plus a nitro-aromatic, and to four pesticides. They established that:

- Stainless steel could be properly cleaned using a hot detergent wash,
- PVC could be properly cleaned using a hot detergent wash,
- PTFE, LDPE, and the more adsorptive polymers, needed a hot detergent wash plus drying in a hot oven.
- a solvent rinse (a recommended procedure in earlier protocols) did not aid in the removal of VOCs from these latter materials.

A few rules that have been established for decontamination of sampling equipment at sensitive sites are:

- Avoid using adsorptive materials for sampling devices and any equipment that is in contact with the water prior to sample collection.
- Include a hot detergent wash and oven drying in the decontamination procedure.
- You can remove “rinsing in a solvent” as part of the decontamination procedure.
- The optimum will be to have dedicated sampling equipment for each sampling point.

If you are about to embark on a sampling program at a sensitive site you will need to obtain and study the ASTM procedure (ASTM 2002), or obtain the USGS procedure (Wilde 2004).

18.4 REFERENCES

ASTM 2002. Standard practice for decontamination of field equipment used at non-radioactive waste sites. Document D5088-02. URL: http://www.astm.org/cgi-bin/SoftCart.exe/DATABASE.CART/REDLINE_PAGES/D5088.htm?L+mystore+meyo0623 (last accessed on 5 November 2006)

Parker, L.V. and Ranney T.A. 1997a. Decontaminating materials used in groundwater sampling devices. Cold Regions Research and Engineering Laboratory, Special Report 97-24. URL: http://www.crrel.usace.army.mil/techpub/ CRREL_Reports/reports/SR97_24.pdf (last accessed on 5 November 2006).

Parker, L.V. and Ranney T.A. 1997b. Decontaminating groundwater sampling devices. Cold Regions Research and Engineering Laboratory, Special Report 97-25. URL: http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR97_25.pdf (last accessed on 5 November 2006).

Wilde, F.D. 2004. Cleaning of Equipment for water sampling (version 4/2004): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3. Obtainable from http://pubs.water.usgs.gov/twri9A3/ (last accessed on 22 November 2006).

CHAPTER 19

SAMPLING OF WETLANDS, SPRINGS AND GROUNDWATER SEEPS

19.1 SAMPLING WETLANDS

There is an increasing awareness of the role that springs, seeps and wetlands play in the maintenance of various ecosystems, and this area of groundwater science is called Groundwater Dependant Ecosystems. As a consequence some sampling programs will include springs, seeps and wetlands. Many, if not most wetlands, are maintained by groundwater in-flow. In order to collect samples of this groundwater great care must be taken to ensure that the water being sampled is actually groundwater flowing into or towards the wetland, and that it is not either surface water or groundwater that has already entered the wetland and which should now be regarded as surface water. So, ensure that the boreholes, seepages or well-points do, in fact, sample the water that they are intended to sample.

19.2 SAMPLING 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 well-pointing spear. This is a short section of stainless steel well-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 piezometers should be installed. Ensure the Monitoring Program Guide has detailed instructions and maps on how to access these wellpoint. Wetlands are eco-sensitive, and random walking will cause damage.

19.3 SAMPLING GROUNDWATER SEEPS

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.

19.4 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 well pointing spear and drive this into the sand close to the pit and collect the sample from this piezometer.

19.5 SAMPLING LARGE DIAMETER DUG WELLS

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 well and start purging. Observe the flow in the well 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 well 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.

CHAPTER 20

THE LAST CHAPTER

20.1 WATER QUALITY GUIDELINES – WEBSITES

The URL addresses below are listed because they have been providing useful information at various times and may still be useful in the future. As with all websites, be aware that they may become outdated and that more recent information may exists elsewhere.

South Africa
http://www.dwaf.gov.za/Dir_WQM/docsFrame.htm (last accessed on 17 October 2006)

World Health Organisation
http://www.who.int/water_sanitation_health/dwq/guidelines/en/index.html (last accessed on 5 November 2006)
http://www.who.int/water_san itation_health/GDWQ/PDF_DOCS/gdw3.pdf. (last accessed on 5 November 2006)

USA
www.epa.gov/OGWDW/mcl.html. (last accessed on 5 November 2006)

Australia and New Zealand
http://www.mfe.govt.nz/publications/water/anzecc-water-quality-guide-02/ (last accessed on 5 November 2006)

United Kingdom
www.dwi.gov.UK./regs/si1147/index.htm (last accessed on 5 November 2006)

European Union
Council Directive 98/83/ED of 3 November 1998 (European Union)
URL: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31998L0083:EN:HTML (last accessed on 5 November 2006)
http://ec.europa.eu/environment/enlarg/handbook/water.pdf (last accessed on 5 November 2006)

APPENDIX A: Tables relevant to Eh field determination (chapter 4.4)

Appendix A: Table 1.
Half-cell potentials (mV) of silver:silver chloride and calomel reference electrodes relative to the standard hydrogen electrode as a function of temperature and potassium chloride filling solution concentration (adapted from Nordström and Wilde 2005). The linear regression equation for each Eh-temperature relationship is also given for interpolation to other temperatures in this range.

	Silver:silver chloride			Calomel			
Temp (°C)	3M KCl	3.5M KCl	Saturated KCl	3M KCl	3.5M KCl	4M KCl	Saturated KCl
10	+220	+215	+214	+260	+256	+255	+254
15	+216	+212	+209	+259	+254	+252	+251
20	+213	+208	+204	+257	+252	+249	+248
25	+209	+205	+199	+255	+250	+246	+245
30	+205	+201	+194	+253	+248	+244	+241
35	+202	+197	+189	+251	+246	+241	+238
40	+198	+193	+184	+249	+244	+239	+234
$E_{1/2\ cell}$ =	-0.73 t + 227	-0.74 t + 223	- t + 224	-0.37 t + 264	-0.4 t + 260	-0.53 t + 260	-0.66 t + 261

Appendix A: Table 2.
Temperature dependence of Eh (platinum electrode vs SHE) for common reference solutions.

Temperature (°C)	Quinhydrone pH 4 (mV)	Quinhydrone pH 7 (mV)	Zobell's (mV)
5	+479	+314	+472
10	+475	+307	+461
12	+474	+304	+457
14	+472	+301	+452
15	+471	+300	+450
16	+471	+299	+448
18	+469	+296	+443
20	+467	+293	+439
22	+466	+290	+435
24	+464	+288	+430
25	+464	+286	+428
26	+463	+285	+426
28	+461	+282	+421
30	+460	+279	+417
35	+456	+272	+406
40	+452	+265	+395

Appendix A: Table 3

Quick reference look up table for theoretical redox potentials of common Eh reference solutions relative to different types of reference electrodes. This is a combination of tables 1 and 2.

Quinhydrone pH 4	Silver/silver chloride			Calomel			
Temperature	**3M KCl**	**3.5M KCl**	**Sat. KCl**	**3M KCl**	**3.5M KCl**	**4M KCl**	**Sat. KCl**
10	+255	+260	+261	+215	+219	+221	+221
15	+255	+259	+262	+213	+217	+220	+220
20	+254	+259	+263	+210	+215	+218	+219
25	+255	+259	+265	+209	+214	+218	+219
30	+255	+259	+266	+207	+212	+216	+219
35	+254	+259	+267	+204	+210	+215	+218
40	+254	+259	+268	+203	+208	+213	+218
Quinhydrone pH 7	**Silver/silver chloride**			**Calomel**			
Temperature	**3M KCl**	**3.5M KCl**	**Sat. KCl**	**3M KCl**	**3.5M KCl**	**4M KCl**	**Sat. KCl**
10	+87	+92	+93	+47	+51	+52	+53
15	+84	+88	+91	+42	+46	+48	+49
20	+80	+85	+89	+36	+41	+44	+45
25	+77	+81	+87	+31	+36	+40	+41
30	+74	+78	+85	+26	+31	+35	+38
35	+70	+75	+83	+21	+26	+31	+34
40	+67	+72	+81	+16	+21	+26	+31
Zobell	**Silver/silver chloride**			**Calomel**			
Temperature	**3M KCl**	**3.5M KCl**	**Sat. KCl**	**3M KCl**	**3.5M KCl**	**4M KCl**	**Sat. KCl**
10	+241	+246	+247	+201	+205	+206	+207
15	+234	+238	+241	+192	+196	+198	+199
20	+226	+231	+235	+182	+187	+190	+191
25	+219	+223	+229	+173	+178	+182	+183
30	+212	+216	+223	+164	+169	+173	+176
35	+204	+209	+217	+155	+160	+165	+168
40	+197	+202	+211	+146	+151	+156	+161

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APPENDIX B:

TABLES TO DETERMINE THE DISSOLVED OXYGEN CONTENT OF WATER.

To use these tables:

- Use the water temperature and either the air pressure (in mBar) or the site elevation amsl (in metres) from either Table 1 or Table 2 to obtain the solubility of oxygen in water (in mg/L).
- If EC > 200 mS/m then read of the correction factor from Table 3 and multiply this with the solubility obtained above.

Example calculation of saturated DO:
At 22^{o} C and 1400 masl and EC = 4000 mS/m ;
DO of water saturated with air will be:
7.4 * 0.86 = 6.4 mg/L = 199 µmole/L

Appendix B: Table 1.
Dissolved oxygen content of water (in mg/L) at different temperatures and pressures in equilibrium with saturated air (derived from Weiss 1970).

Pressure (mBar)	**1020**	**1000**	**980**	**960**	**940**	**920**	**900**	**880**	**860**	**840**	**820**	**800**	**780**
Temp(^{o} C)													
0	14.7	14.4	14.1	13.8	13.5	13.3	13.0	12.7	12.4	12.1	11.8	11.5	11.2
2	13.9	13.6	13.4	13.1	12.8	12.5	12.3	12.0	11.7	11.4	11.2	10.9	10.6
4	13.2	12.9	12.7	12.4	12.1	11.9	11.6	11.4	11.1	10.9	10.6	10.3	10.1
6	12.5	12.3	12.0	11.8	11.5	11.3	11.0	10.8	10.6	10.3	10.1	9.8	9.6
8	11.9	11.7	11.4	11.2	11.0	10.7	10.5	10.3	10.0	9.8	9.6	9.3	9.1
10	11.3	11.1	10.9	10.7	10.5	10.2	10.0	9.8	9.6	9.3	9.1	8.9	8.7
12	10.8	10.6	10.4	10.2	10.0	9.8	9.6	9.3	9.1	8.9	8.7	8.5	8.3
14	10.4	10.2	10.0	9.8	9.5	9.3	9.1	8.9	8.7	8.5	8.3	8.1	7.9
16	9.9	9.7	9.5	9.3	9.1	8.9	8.8	8.6	8.4	8.2	8.0	7.8	7.6
18	9.5	9.3	9.1	9.0	8.8	8.6	8.4	8.2	8.0	7.8	7.6	7.5	7.3
20	9.1	9.0	8.8	8.6	8.4	8.2	8.1	7.9	7.7	7.5	7.3	7.2	7.0
22	8.8	8.6	8.4	8.3	8.1	7.9	7.7	7.6	7.4	7.2	7.1	6.9	6.7
24	8.5	8.3	8.1	8.0	7.8	7.6	7.5	7.3	7.1	7.0	6.8	6.6	6.5
26	8.1	8.0	7.8	7.7	7.5	7.3	7.2	7.0	6.9	6.7	6.5	6.4	6.2
28	7.9	7.7	7.5	7.4	7.2	7.1	6.9	6.8	6.6	6.5	6.3	6.2	6.0
30	7.6	7.4	7.3	7.1	7.0	6.8	6.7	6.5	6.4	6.2	6.1	6.0	5.8
32	7.3	7.2	7.0	6.9	6.8	6.6	6.5	6.3	6.2	6.0	5.9	5.8	5.6
34	7.1	7.0	6.8	6.7	6.5	6.4	6.3	6.1	6.0	5.8	5.7	5.6	5.4
36	6.9	6.7	6.6	6.5	6.3	6.2	6.1	5.9	5.8	5.7	5.5	5.4	5.3
38	6.7	6.5	6.4	6.3	6.1	6.0	5.9	5.7	5.6	5.5	5.3	5.2	5.1
40	6.5	6.3	6.2	6.1	5.9	5.8	5.7	5.6	5.4	5.3	5.2	5.1	4.9

Appendix B: Table 2

Dissolved oxygen content of water (in mg/L) at different temperatures and elevations in equilibrium with saturated air (derived from Weiss 1970).

Elevation (m)	0	200	400	600	800	1000	1200	1400	1600	1800	2000	2200
Temp(^{o} C)												
0	14.6	14.2	13.9	13.6	13.3	12.9	12.6	12.3	12.1	11.8	11.5	11.2
2	13.8	13.5	13.2	12.8	12.5	12.3	12.0	11.7	11.4	11.1	10.9	10.6
4	13.1	12.8	12.5	12.2	11.9	11.6	11.3	11.1	10.8	10.6	10.3	10.1
6	12.4	12.1	11.8	11.6	11.3	11.0	10.8	10.5	10.3	10.0	9.8	9.6
8	11.8	11.5	11.3	11.0	10.7	10.5	10.2	10.0	9.8	9.5	9.3	9.1
10	11.3	11.0	10.7	10.5	10.2	10.0	9.8	9.5	9.3	9.1	8.9	8.7
12	10.8	10.5	10.3	10.0	9.8	9.5	9.3	9.1	8.9	8.7	8.5	8.3
14	10.3	10.0	9.8	9.6	9.4	9.1	8.9	8.7	8.5	8.3	8.1	7.9
16	9.9	9.6	9.4	9.2	9.0	8.7	8.5	8.3	8.1	7.9	7.8	7.6
18	9.4	9.2	9.0	8.8	8.6	8.4	8.2	8.0	7.8	7.6	7.4	7.3
20	9.1	8.9	8.6	8.4	8.2	8.0	7.9	7.7	7.5	7.3	7.1	7.0
22	8.7	8.5	8.3	8.1	7.9	7.7	7.6	7.4	7.2	7.0	6.9	6.7
24	8.4	8.2	8.0	7.8	7.6	7.4	7.3	7.1	6.9	6.8	6.6	6.5
26	8.1	7.9	7.7	7.5	7.4	7.2	7.0	6.8	6.7	6.5	6.4	6.2
28	7.8	7.6	7.4	7.3	7.1	6.9	6.8	6.6	6.4	6.3	6.1	6.0
30	7.5	7.4	7.2	7.0	6.8	6.7	6.5	6.4	6.2	6.1	5.9	5.8
32	7.3	7.1	6.9	6.8	6.6	6.5	6.3	6.2	6.0	5.9	5.7	5.6
34	7.0	6.9	6.7	6.6	6.4	6.3	6.1	6.0	5.8	5.7	5.5	5.4
36	6.8	6.7	6.5	6.3	6.2	6.1	5.9	5.8	5.6	5.5	5.4	5.2
38	6.6	6.5	6.3	6.2	6.0	5.9	5.7	5.6	5.5	5.3	5.2	5.1
40	6.4	6.3	6.1	6.0	5.8	5.7	5.6	5.4	5.3	5.2	5.0	4.9

Appendix B: Table 3

Correction factors to calculate the salinity effect on DO in water (in mg/L) (derived from Weiss 1970)

EC (mS/m)	0	200	500	1000	2000	3000	4000	5000	6000	7000	8000	9000	10 000
Temp(^{o} C)													
0	1.00	0.99	0.98	0.96	0.92	0.88	0.84	0.80	0.76	0.72	0.68	0.63	0.59
2	1.00	0.99	0.98	0.96	0.92	0.88	0.84	0.80	0.76	0.72	0.68	0.64	0.60
4	1.00	0.99	0.98	0.96	0.92	0.89	0.85	0.80	0.76	0.72	0.68	0.64	0.60
6	1.00	0.99	0.98	0.96	0.93	0.89	0.85	0.81	0.77	0.73	0.69	0.65	0.61
8	1.00	0.99	0.98	0.96	0.93	0.89	0.85	0.81	0.77	0.73	0.69	0.65	0.61
10	1.00	0.99	0.98	0.96	0.93	0.89	0.85	0.81	0.77	0.73	0.69	0.66	0.62
12	1.00	0.99	0.98	0.96	0.93	0.89	0.85	0.81	0.78	0.74	0.70	0.66	0.62
14	1.00	0.99	0.98	0.97	0.93	0.89	0.86	0.82	0.78	0.74	0.70	0.66	0.63
16	1.00	0.99	0.98	0.97	0.93	0.89	0.86	0.82	0.78	0.74	0.70	0.67	0.63
18	1.00	0.99	0.98	0.97	0.93	0.90	0.86	0.82	0.78	0.75	0.71	0.67	0.63
20	1.00	0.99	0.98	0.97	0.93	0.90	0.86	0.82	0.79	0.75	0.71	0.67	0.64
22	1.00	0.99	0.98	0.97	0.93	0.90	0.86	0.83	0.79	0.75	0.72	0.68	0.64
24	1.00	0.99	0.98	0.97	0.93	0.90	0.86	0.83	0.79	0.76	0.72	0.68	0.65
26	1.00	0.99	0.98	0.97	0.94	0.90	0.87	0.83	0.79	0.76	0.72	0.69	0.65
28	1.00	0.99	0.98	0.97	0.94	0.90	0.87	0.83	0.80	0.76	0.73	0.69	0.65
30	1.00	0.99	0.98	0.97	0.94	0.90	0.87	0.84	0.80	0.76	0.73	0.69	0.66
32	1.00	0.99	0.98	0.97	0.94	0.91	0.87	0.84	0.80	0.77	0.73	0.70	0.66
34	1.00	0.99	0.99	0.97	0.94	0.91	0.87	0.84	0.81	0.77	0.74	0.70	0.67
36	1.00	0.99	0.99	0.97	0.94	0.91	0.87	0.84	0.81	0.77	0.74	0.70	0.67
38	1.00	0.99	0.99	0.97	0.94	0.91	0.88	0.84	0.81	0.78	0.74	0.71	0.67
40	1.00	0.99	0.99	0.97	0.94	0.91	0.88	0.85	0.81	0.78	0.75	0.71	0.68

APPENDIX C Table 1. Sample size, preservation and holding time for various determinands.

These details are mere guideline based on past experience of the authors. In all cases consult the analytical laboratory prior to sampling and follow their recommendations.

Measurement	Volume required (ml)	Container plastic (P) or glass (G)	Preservation	Maximum holding time
Acidity	100	P/G	Cool, 4°C	24 hrs
Alkalinity	200	P/G	Cool, 4°C	24 hrs
Aluminium	50	P(A)/G(A)	Membrane filter on site, HNO_3 to pH<2	6 months
Ammonium	500	P/G	Cool, 4°C H_2SO_4 to pH<2	24 hours 7 days
Arsenic	100	P(A)/G(A)	Filter on site, HNO_3 to pH<2	6 months
Boron	1000	P(PTFE) or quartz	HNO_3 to pH<2	28 days
Bromide	100	P/G	Cool, 4°C	28 days
BTEX			See VOCs	
Calcium	100	P(A)/G(A)	Filter on site, HNO_3 to pH<2	6 months
$\delta^{13}C$	100	P/G	NaN_2	3 months
^{14}C	20-100 litre	P/G	Extract carbonate on site	1 year
^{14}C	200	G		6 months
CFCs	100	Special containers		3 months
COD	100	G preferred	H_2SO_4 to pH<2 Cool, 4°C	7 days
Chloride	50	P/G	Cool, 4°C	28 days
Colour	500	P/G	Cool, 4°C	48 hours
Chromium total hexavalent	 100 1000	 P(A)/G(A) P(A)/G(A)	 Filter on site, HNO_3 to pH<2 Unfiltered, Cool, 4°C	 6 months 24 hours
Cyanide total	1000	P/G	NaOH to pH>12 Cool, 4°C, Dark	14 days 24 h if S^{2-} present
Deuterium	20	P/G	-	1 year

Diesel Range Organics (DRO)	1000	G, TC	Cool, 4°C	7 days (40 days extracted)
DO: Winkler	300	G	Fix on site	8 hours
DOC	100	G preferred	Cool, 4°C, Dark	7 days
EC	500	P/G	None	28 days
Fluoride	100	P/G	None	28 days
Gasoline Range Organics	40 x 2	G, TC	Cool, 4°C	14 days
Hardness	100	P/G	Cool, 4°C HNO_3 to pH<2	7 days 6 months
Iodine	500	P/G	Unfiltered, Cool, 4°C	24 hours
Iron: total Iron: ferrous	50 50	P(A)/G(A) P(A)/G(A)	Filter on site HNO_3 to pH<2 Analyse on site	6 months 15 min
Manganese	50	P(A)/G(A)	Filter on site, HNO_3 to pH<2	6 months
Major cations & anions	500	P/G	Cool, 4°C	7 days
Metals (not Hg or Cr (VI)	1000	P(A)/G(A)	Filter on site HNO_3 to pH<2	6 months
Mercury	500	G(A)/P(A)	Filter on site HNO_3 to pH<2 Cool, 4°C	28 days (G) 14 days (P)
Microbiology Coliforms Plate count	 1000 100	G(B)/P, sterilized	Cool, <10°C during transit	 24 hours 24 hours
MTBE			see VOCs	
Nitrate	100	P/G	Cool, 4°C, dark H_2SO_4 to pH<2	1-2 days
Nitrite	100	P/G	Cool, 4°C, dark	ASAP
$\delta^{15}N$	500	P/G	Cool, Chloroform or H_2SO_4	2 months
Organic N (Kjeldahl)	500	P/G	Cool, 4°C H_2SO_4 to pH<2	7 days
Oil & grease	1000	G, wide mouth calibrated	Cool, 4°C H_2SO_4 to pH<2	24 hours 28 days
$\delta^{18}O$	20	P/G	-	1 year
Pesticides &	1000	G(S), Amber, TC	Cool, 4°C, Dark	7 days

PCBs				(40 days extracted)
Ph	50	P/G	Analyse on site	15 min
Phenolics	500	G/P, TC	Cool, 4°C H_2SO_4 to pH<2	28 days
PAHs	1000	G(S), Amber, TC	Cool, 4°C, Dark	7 days (40 days extracted)
Parasites	Filtered on site, 100 to 1000 L	Filter stored in plastic	Cool, 4°C	4 days
Phosphorus Total	100	P/G	Cool, 4°C H_2SO_4 to pH<2	28 days
Orthophosphate	100	G(A)	Filter on site Cool, 4°C	48 hours
Radioactivity Gross alpha Gross beta Radium 226 Radium 228 Radon 222 Uranium Caesium Strontium Iodine Photon-emitters	 >1000 >1000 >1000 >1000 2 x 25 >1000 >1000 >1000 >2000 >1000	 P/G P/G P/G P/G Special containers P/G P/G P/G P/G P/G	 HNO_3 to pH<2 HNO_3 to pH<2 HNO_3 to pH<2 HNO_3 to pH<2 Cool, 4°C HNO_3 to pH<2 HCl to pH<2 HNO_3 to pH<2 None HNO_3 to pH<2	 1 year 1 year 1 year 1 year 4 days 1 year 1 year 1 year 14 days 1 year
Potassium	100	P/G(B)	Filter on site, HNO_3 to pH<2	6 months
Semi VOCs	1000	G(S), Amber, TC	Cool, 4°C	7 days (40 days extracted)
Selenium	100	P(A)/G(A)	Filter on site, HNO_3 to pH<2	6 months
SF_6	200	Special containers	-	2 months
Silica	200	P (PTFE) or quartz	Cool, 4°C. Do not freeze	28 days
Sodium	100	P	Cool, 4°C	6 months
Sulphate	100	P/G	Cool, 4°C	28 days
Sulphide	100	P/G	Cool, 4°C, 4 drops Zn acetate/100 mL + NaOH to pH>9	28 days
Surfactants	250	P/G	Cool, 4°C	48 hours

(MBAS)				
Temperature	50	P/G	Analyse on site	15 min
Tritium	500	G	None	1 year
Turbidity	100	P/G	Cool, 4°C, Dark	24 hours
THM	1000 2 x 25	G, TC G, TC	Cool, 4 C Cool, 4 C	24 hours 14 days
TPH	1000	G, TC	Cool, 4°C, Add 5 ml 50% HCl	28 days
Viruses	100 to 1000 L	Filtered on site Filter stored in plastic	Cool, 4°C	4 days
VOC	2 x 40	G, TC	Cool, 4°C HCl to pH<2	14 days

(A) acid rinsed with 1+1 HNO_3 (B) borosilicate glass
(S) organic solvent rinsed (reagent grade acetone or methylene chloride) or baked
TC Teflon lined cap