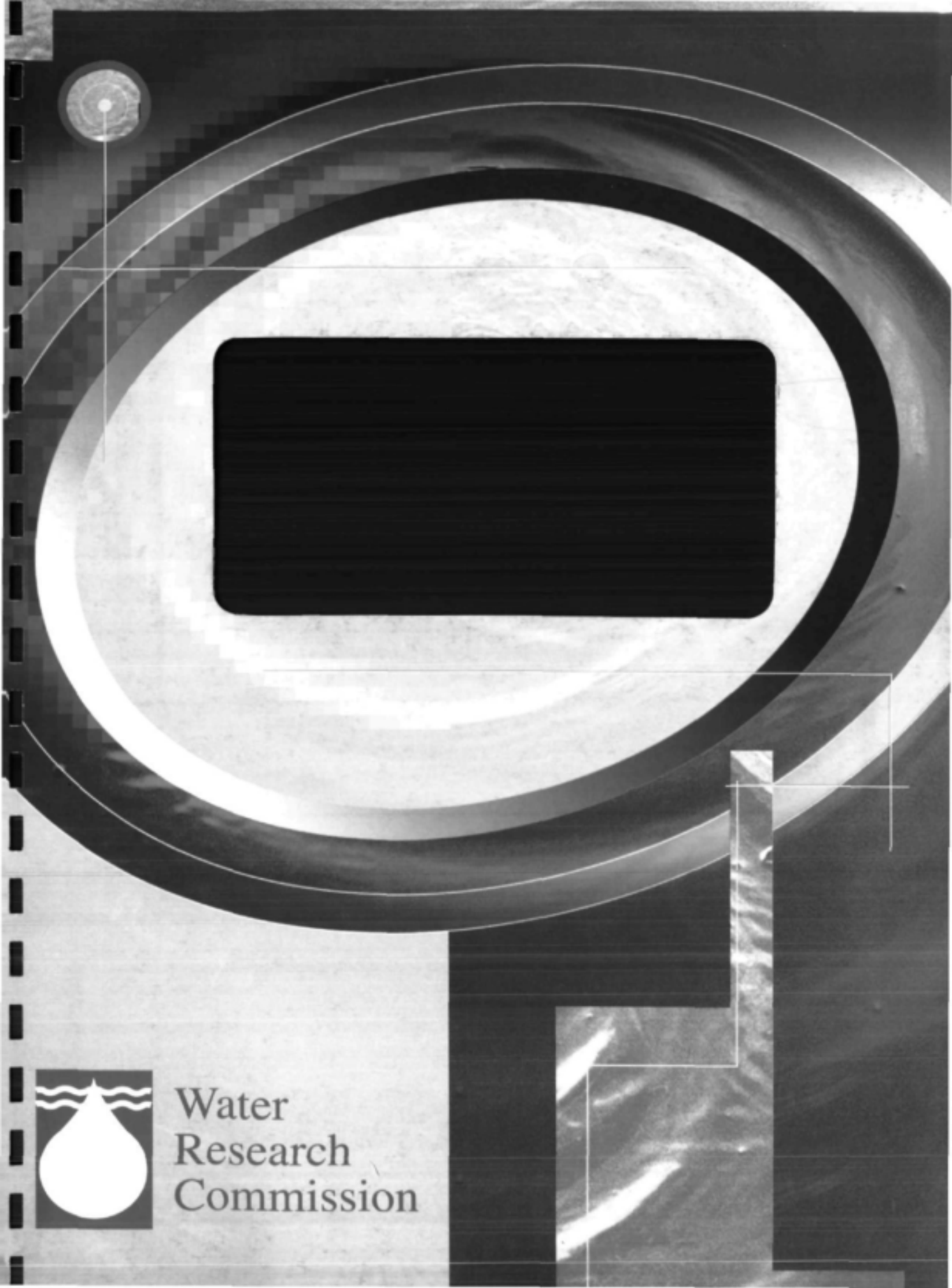

Water
Research
Commission

GROUNDWATER SAMPLING
A Comprehensive Guide for Sampling Methods

By John M. C. Weaver

WRC Report No TT 54/92

GROUNDWATER SAMPLING

A COMPREHENSIVE GUIDE FOR SAMPLING METHODS

Prepared for the
Water Research Commission

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INDEX

CHAPTER 5 - FIELD DETERMINANDS

CHAPTER 11 - SAMPLE COLLECTING DEVICES

CHAPTER 12 - PURGING THE BOREHOLE

CHAPTER 13 - FILTERING DEVICES

CHAPTER 14 - FLOW-THROUGH CELL

CHAPTER 15 - MULTIPLE LEVEL SAMPLING

CHAPTER 16 - PROTECTIVE CLOTHING

CHAPTER 17 - DECONTAMINATION

CHAPTER 1

INTRODUCTION

The purpose of this manual 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 be **RELIABLY** used to evaluate hydrogeochemical conditions.

The manual is presented in two volumes. Volume 1 is the complete manual comprising Chapters 1 to 21. As the manual is comprehensive and bulky it is impractical for field use. Volume 2 is an abbreviated version intended for field use and comprises Chapters 2, 3 and 7 of Volume 1. The user of Volume 2 must ideally first have read and understood Volume 1.

Chapter 2 is a summary of the manual. Three tables in matrix form are presented. From Table 2-1, according to the field of investigation which is either groundwater consumption, groundwater hydrochemistry survey or groundwater pollution monitoring, one can determine those field determinands and laboratory determinands that need to be measured. Table 2-2 shows which sample collecting device may be used for various determinands. Table 2-3 provides preservation details for the determinands that will be measured by the laboratory.

Chapter 3 is about planning a sampling run and includes a check-list of procedures, equipment and the field method which, if followed closely, will reduce the possibility of omitting any vital steps.

Chapter 4 is a description of all the various determinands that a hydrogeologist would measure 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 5 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.

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

Chapters 9 to 18 describe various devices and procedures used or followed in a groundwater monitoring programme.

Chapter 19 comprises two tables of drinking-water quality criteria.

Chapter 20 is a list of abbreviations used in groundwater quality investigations.

Chapter 21 is a comprehensive list of the recommended reading. Certain books were extensively used in the preparation of this manual, the three most used being APHA (1989), Everett (1980) and Gillham *et al.* (1983).

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

To round off this introduction here are a few "wise" sayings.

THERE IS NO EXCUSE FOR COLLECTING A SAMPLE WHICH DUE TO ITS METHOD OF COLLECTION GIVES ERRONEOUS 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.

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CHAPTER 2

SUMMARIZED SAMPLING GUIDE

This chapter contains three reference tables:

Table 2.1 - The *sampling tree*
Table 2.2 - *Sample collection devices* that are suitable for collecting the various groundwater parameters (from Chapter 11).
Table 2.3 - *Table of water sample volume required, sample container, preservation, holding time and American Public Health Association (APHA) method.*

The *sampling tree* is a reference table. Having established for what purpose you need to know the water-quality, by cross-referencing you can obtain the field determinands that must be measured and the determinands that must be analysed.

The matrix of sample collection devices shows what pump, bailer or other equipment you may use to collect the water sample with minimum bias.

Once you know from the sampling tree which determinands must be analysed, look up in the summary table to determine the sample volume required, sample bottle type, preservation method, maximum holding time and the APHA Standard Method Number.

Note that this chapter is a summary of the whole manual and should only be used/ consulted if you have read and understood the entire manual.

Table 2.1 Sampling tree

		FIELD MEASUREMENT[1]	DETERMINANDS TO BE MEASURED IN THE LABORATORY
WATER QUALITY FOR CONSUMPTION	HOUSEHOLD CONSUMPTION	pH (Alkalinity)	CAT/AN[2] Microbiology[3] Fe/Mn and other elements if a problem is suspected e.g. encrustation/corrosion.
	LIVESTOCK DRINKING	pH & EC	F & NO_3 if a problem is suspected
	IRRIGATION	pH (Alkalinity)	CAT/AN, Fe/Mn, encrustation/corrosion
	INDUSTRIAL USAGE	pH Eh ALKALINITY	CAT/AN, encrustation/corrosion, Fe/Mn.
HYDROCHEMISTRY FOR GROUNDWATER SURVEYS	MAJOR HYDROCHEMISTRY	pH Eh ALKALINITY	CAT/AN plus what project needs.
	TRACE ELEMENTS	pH Eh ALKALINITY	CAT/An plus trace elements as project needs.
	RADIO ISOTOPES		Determined by project
	ARTIFICIAL RECHARGE	pH Eh	K, NO_3 plus what project indicates is needed.
GROUNDWATER POLLUTION MONITORING	CLASS 1 WASTE DISPOSAL	pH Eh ALKALINITY	CAT/AN, DOC[4], DOX[5] plus toxic substances of interest
	CLASS 2 WASTE DISPOSAL	pH Eh ALKALINITY	CAT/AN, DOC, DOX plus toxic substances of interest
	CLASS 3 WASTE DISPOSAL	pH Eh ALKALINITY	CAT/AN, DOC plus toxic substances of interest, if any.
	PESTICIDE CONTAMINATION	pH	Identified target pesticides, nitrate and potassium.
	ACID MINE DRAINAGE (AMD)	pH Eh ALKALINITY	CAT/AN, identified heavy metals.
	SEWAGE DISPOSAL	pH Eh ALKALINITY	CAT/AN, DOC microbiology
	ARTIFICIAL RECHARGE	pH Eh	CAT/AN, DOC microbiology, phenols and DOX
	UNDERGROUND STORAGE TANKS (UST)	pH Eh ALKALINITY	DOC, Identified substances plus degradation products.
	GENERAL SUSPECTED POLLUTION	pH Eh ALKALINITY	CAT/AN, DOC, DOX

1. Temperature is measured as a matter of course when measuring pH.
2. CAT/AN - Full analysis of major cations and anions.
3. Microbiology - Includes the standard determinands for drinking-water quality.
4. DOC - Dissolved organic carbon
5. DOX - Dissolved organic halogens

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 rocks or multilevel aquifers may call for in situ sampling devices as indicated [illegible].

		Device	Approximate Maximum Sample Depth	Minimum Well Diameter	Sample Delivery Rate of Volume	GROUND WATER PARAMETERS: INORGANIC* EC	pH	Redox	Major Ions	Trace Metals	Nitrate Fluoride	Dissolved gases	ORGANIC* Non-volatile	Volatile	TOC	TOX	RADIOACTIVE Radium	Gross alpha & beta	BIOL 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	200 ft	50 mm	0 - 2 L/min									*					
		Bladder pump	400 ft	38 mm	0 - 7.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	*
		Helical rotor	160 ft	50 mm	0 - 4.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	
		Piston pump (gas-drive)	500 ft	38 mm	0 - 2 L/min	*			*	*	*		*				*	*	
		Centrifugal	Variable	75 mm	variable	*			*		*						*	*	
	SUCTION LIFT	Peristaltic	26 ft	12 mm	0.04 - 1.1 L/min	*			*		*		*				*		*
	GAS CONTRACT	Gas lift	variable	25 mm	variable														
		Gas-drive	150 ft	25 mm	0.75 L/min	*			*		*		*				*		
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 device construction materials (including tubing, lead lines, etc.) should be evaluated for suitability in analyzing specific groundwater parameters. It is assumed in this chart that existing monitoring wells are properly installed and constructed of materials suitable for detection of the parameters of interest. See references for additional information.

Sample 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, rate should be carefully controlled to prevent aeration or degassing of the sample.

* Indicates device is generally suitable for application [illegible] (and is constructed of suitable materials).

Table 2.2 Sample collecting devices (see Chapter 11)

Table 2.3 Sample size, preservation and holding time

Measurement	Volume required (mL)	Container plastic or glass Teflon-cap	Preservation	Maximum holding time	APHA Standard Method Number
Acidity	100	P,G	Cool, 4°C	24 hrs	2310 - Acidity
Alkalinity	100	P,G	Cool, 4°C	24 hrs	2320 - Alkalinity
Aluminium	50	P,G	Filter on site HNO_3 to pH < 2	6 months	3111
Arsenic	100	P,G	HNO_3 to pH < 2	6 months	3114 - metals by Hydride generation/AAS
Bromide	100	P,G	Cool, 4°C	24 hrs	4500 - Br^-
COD	50	P,G	H_2SO_4 to pH < 2	7 days	5220 - COD
Chloride	50	P,G	None	7 days	4500 - Cl^-
Colour	50	P,G	Cool, 4°C	24 hrs	2120 - Colour
Chromium	100	P,G	Filter on site	6 months	3500
Cyanides	500	P,G	Cool, 4°C NaOH to pH12	24 hrs	4500 - CN^-
Dissolved oxygen					
Probe	300	G only	Det. on site	None	4500 - O Oxygen (dissolved)
Winkler	300	G only	Fix. on site	None	4500 - O Oxygen (dissolved)
DOC	100	P,G	Cool, 4°C	14 days	5310
DOX	50	G,T-cap	Cool, 4°C HNO_3 to pH < 2	14 days	5320
Fluoride	300	P,G	Cool, 4°C	7 days	4500 - F^- Fluoride
Hardness	100	P,G	Cool, 4°C	7 days	2340 - Hardness
Iodine	100	P,G	Cool, 4°C	24 hrs	4500 - I Iodine
Iron	50	P,G	Filter on site HNO_3 to pH < 2	6 months	3500-Fe
Manganese	50	P,G	Filter on site HNO_3 to pH < 2	6 months	3500-Mn
Metals					
Dissolved	200	P,G	Filter on site HNO_3 to pH < 2	6 months	3010 - 3500
Mercury					3112
Dissolved	100	P,G	Filter HNO_3 to pH < 2	38 days (glass) 13 days (plastic)	

Always mark on the sample bottle the preservative used.

Table 2.3 (cont.)

Measurement	Volume required (mL)	Container plastic or glass Teflon-cap	Preservation	Maximum holding time	APHA Standard Method Number
Nitrogen					4500 - N
Ammonia	400	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 hrs	4500 - NH_3
Kjeldahl	500	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 hrs	4500 - Norg
Nitrate	100	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 hrs	4500$^-$ NO_3^-
Nitrite	50		Cool, 4°C	24 hrs	4500$^-$ NO_2^-
Oil & grease	1 000	G only	Cool, 4°C H_2SO_4 to pH < 2	24 hrs	5520 Oil and grease
Pesticides	1000	G,T-cap	Cool, 4°C	14 days	6000 - 6640
pH			Det. on site		4500 - H^+
Phenols	1000	G,T-cap	Cool, 4°C H_2SO_4 pH < 2	28 days	5530 Phenols
Phosphorus					
Ortho-phosphate, dissolved	50	P,G	Filter on site Cool, 4°C	24 hrs	4500 - P
Hydrolyzable	50	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 hrs	4500-P
Total, dissolved	50	P,G	Filter on site Cool, 4°C	24 hrs	4500-P
Radioactivity	5000	P	Filter on site 5 mL HNO_3 per 1 L	48 hrs	
Radon	100	G, T-cap	Cool, 4°C	24 hrs	
Selenium	50	P,G	HNO_3 to pH < 2	6 months	3114
Silica	50	P only	Cool, 4°C	7 days	4 500 - Si
Sulfate	50	P,G	Cool, 4°C	7 days	4500 - SO_4^{2-}
Sulfide	50	P,G	2 ml zinc acetate	24 hrs	4500 - S^{2-}
Sulfite	50	P,G	Cool, 4°C	24 hrs	4500 - SO_3^{2-}
Trihalomethanes	2 x 25	G,T-cap	a) Cool, 4°C b) Cool, 4°C Chlorine	14 days	6232
VOC	2 x 50	G,T-cap	Cool, 4°C	14 days	6210

CHAPTER 3

PLANNING A SAMPLING RUN

3.1 PLANNING THE SAMPLING PROGRAMME

Possibly the most important step is to *liaise with the analytical laboratory*. Discuss the aims of the project with the laboratory - their input can be invaluable. Establish what determinands need to be identified. Discuss the laboratory's requirements for testing. This will include sample quantities, preservation techniques and time/day to submit sample for analysis. A good working relationship with a laboratory is essential. Establish the standard of work produced by the laboratory and if it is not of a sufficiently high standard consider using another laboratory. Time spent with the laboratory personnel can save many hours of unnecessary work. Liaise before embarking on a pilot sampling run and if necessary, modify techniques if that will produce more accurate results.

Arrange *access* to wells/boreholes to be sampled. This may involve having duplicate keys made. Notify property owners of your intentions to sample. Consider the impact of sampling upon the environment and plan rehabilitation measures. Establish from the client what the liabilities would be, should any damage to property or the environment occur as a result of sampling.

Embark on 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, and anything of relevance which will facilitate efficient 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.

Compile the Monitoring Programme Guide. This should be a detailed document covering every possible aspect of the project. 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, parameters 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 programme monitoring guide regular sampling runs may commence.

3.2 CHECKLIST OF SAMPLING EQUIPMENT REQUIRED IN THE FIELD

1. Map or instructions for locating the sampling site or sites
2. Monitoring Programme Guide
3. Key to get into site and Q20 or oil to lubricate padlocks
4. Water level recorder, distilled water to clean recorder, spare batteries
5. Tape measure, as long as possible
6. Paper towels, rags, plus plastic carrier bag for discards
7. Pump or purging device, power, compressor, clear plastic bailer, if you expect oil
8. Containers for purged water
9. Flow-through cell
10. Thermometer
11. Conductivity meter
12. pH meter, electrode and buffer solutions, spare batteries, thermometer
13. Eh meter, electrode and buffer solution, spare batteries, thermometer
14. DO meter plus reagents
15. Wash bottle (distilled water)
16. Titration kit to test alkalinity/acidity in the field
17. Labels
18. Sample record sheets to identify sample and/or sample sets and to record determinands which are measured in the field
19. Custody sheets
20. Indelible fibre tip pen/s, pencils, ballpoint, field note book, micro-cassette recorder (especially useful for recording field notes in the rain)
21. Sample bottles and caps (foil and Teflon when necessary)
    - Always take more than necessary
    - Cleaned and/or sterilised by laboratory as needed
    - For inorganic chemical analysis
    - For organic chemical analysis
    - For microbiological analysis
    - For virological analysis

NB : Number and size of the bottles depend on determinands being analysed.

22. Bottles containing the various preservatives (clearly labelled) or ampoules of preservative
23. Material to "spike" samples for quality control
24. Trip blanks for VOC samples
25. Filter apparatus for field filtered samples, including extra filters
26. Protective clothing (see Chapter 16 especially on contact lenses). This includes rain gear, warm clothing, sun glasses, sun hat
27. Hose pipe
28. Preservation equipment e.g. ice box/cool box with cooling medium such as cool blocks, ice. Foil to protect those samples sensitive to light
29. Shovel
30. Toolbox
31. Torch
32. Container to measure pumping rate, 25 litre or 10 litre
33. Camera and film
34. First aid kit (commercially available kits)
35. Drop sheet (some type of sheeting to protect instruments from contamination in the event of their falling to the ground)
36. Calculator
37. Personal equipment, money, identity card, credit card, business card (you may meet a potential client), food and drink etc.
38. Decontamination kit, sprays, detergent, buckets, soap, rinse water and PVC pipe
39.
40.
41.
42.
43.
44.
45.
46.
47.
48.
49.
50.

Note Add to this list your own additional items. Photocopy the list and as you pack the truck, tick off on the list what you have packed, so that you do not leave an essential item behind. Pack equipment away thoughtfully taking into consideration the order in which it will be required. Try to keep equipment as clean as possible. Wash with distilled water after use to prevent contamination. Sampling is susceptible to error and this should be kept to a minimum.

3.3 GENERAL GROUNDWATER SAMPLING PROCEDURE

1. Arrive at the sampling site.
2. Consult Monitoring Programme Guide for specific details of the sampling site.
3. Fill in sampling sheet i.e. weather conditions, date, time and sample number or set number.
4. Put down drop sheet to avoid any contamination of equipment, should it fall on the ground.
5. Don protective clothing as required by the site classification.
6. Assemble sample kit at the wellpoint/borehole.
7. Remove any seal on the monitoring point, such as a locking cap or man hole cover.
8. Measure static prepumped water level, record the level and rinse off.
9. Install pump or sample extraction device using data from Monitoring Programme Guide to determine installation depth and type of pump required for the specific site.
10. Purge the hole. Refer to the Monitoring Programme Guide for purging rates and times. If the water in the hole is hazardous collect purged water in a suitable container and remove from site.
11. Measure and record the following field parameters, whilst purging the hole of stagnant water.
    i. temperature
    ii. pH
    iii. Eh and/or DO
    iv. EC
    v. Alkalinity
12. Check 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.
13. Complete the following whilst purging the hole:
    sampling record sheets and log custody forms
    label and/or mark bottles
14. Collect unfiltered samples (see individual section on types of equipment used, methods etc...) Label sample sets as you go along.
15. Collect samples for organic compounds - unfiltered.
16. Collect samples for pesticides - unfiltered.
17. Collect samples for sensitive nonfiltered inorganic compounds (cyanide, ammonia) - unfiltered.
18. Collect sample for microbiology - unfiltered.
19. Collect sample of major cations and anions - unfiltered.
20. Attach in-line filter for sample sets 21 to 23.
21. Determine alkalinity/acidity in the field, aiming for minimal air contact.
22. Collect sample for dissolved trace metals - filtered.
23. Collect sample for phosphate, iron and manganese - filtered.
24. Switch off the pump.

25. Clean all equipment thoroughly before putting it away, rinsing with distilled water where indicated.
26. Complete all necessary forms.
27. Ensure all preservation procedures are complete.
28. Return to laboratory in time for analysis to be started before sample deteriorates. If in a remote area, prepare 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.

3.4 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 the necessary repairs and replace broken equipment.

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 *meters*, do you have in the carrying-case a set of precise step-by-step instructions and are they water-protected? Are your buffer solutions still viable 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?

CHAPTER 4

DETERMINAND SELECTION

4.1 INTRODUCTION

The selection of determinands to be analysed depends on the purpose of the hydrochemical survey. Hydrochemical surveys can be divided into three broad categories:

1. Water quality surveys for consumption
2. Groundwater hydrochemistry surveys
3. Groundwater pollution 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 (Chapter 2).

The selection of these 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.

The determinands can be divided into groups namely:

INORGANIC -
- Major cations and anions
- Phosphate
- Iron and manganese
- Heavy metals
- Trace elements
- Radioactivity
- Encrustation/corrosion

ORGANIC

MORE COMMONLY ENCOUNTERED
- Phenols
- Trihalomethanes (THMs)
- Pesticides
- Petroleum derived compounds

GENERAL GROUPS
- Dissolved organic carbon (DOC)
- Total organic halogen (TOX)
- Volatile organic carbons (VOC)

- Semi-(or non-) volatile organic carbons (NVOC)
- Light non-aqueous phase liquids (LNAPL)
- Dense non-aqueous phase liquids (DNAPL)

MICROBIOLOGICAL

- Standard Plate Count
- Total coliforms
- Faecal coliforms
- *Clostridium perfringens*
- Coliphages
- Enteric virus
- Others

4.2 INORGANIC DETERMINANDS

4.2.1 MAJOR CATIONS AND ANIONS

These are:	K	- potassium
	Na	- sodium
	Ca	- calcium
	Mg	- magnesium
	NH_4	- ammonia
	SO_4	- sulphate
	NO_x	- nitrate (plus nitrite)
	Cl	- chloride
	Alkalinity	- carbonate plus bicarbonate
And also	F	- fluoride
	PO_4	- phosphate

Make sure the sample bottle is clean. Soak for a few days beforehand if feasible. If not, rinse at least three times with water from the sample site (remember to include the cap) before collecting the water sample. Glass or plastic sample bottles can be used, but plastic is preferable as glass can break more easily.

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

On-site filtration is not needed. Note that if phosphate is a critical parameter a filtered sample must be collected. Keep the samples cool, not specifically at 4 °C, but do not leave in the sun.

4.2.2 PHOSPHATE

Phosphate readily precipitates out onto suspended sediment or onto the sides of the sample container. Thus if phosphate is a critical parameter, an on-site filtered sample must be collected.

4.2.3 AMMONIA AND NITRATE

Ammonia in a water sample, which if not chemically preserved, will slowly be degraded by microbiological activity to nitrate. The rate of conversion is variable. If the ratio of ammonia to nitrate is important the bacterial activity must be inhibited by either acidifying the water sample with H_2SO_4 to $pH < 2$ or by adding an ampoule of mercury chloride ($HgCl_2$). Confirm with the laboratory which method is preferred. Ensure the sample bottle is correctly marked.

4.2.4 IRON AND MANGANESE

Iron and manganese above 0,5 mg/L and 0,05 mg/L respectively may cause stains, especially to clothing that has been washed. A high iron concentration also imparts a metallic taste to water.

Iron in solution in groundwater is in the Fe(II) state. When this water comes into contact with air the iron is oxidised to Fe(III) which is insoluble and precipitates as $Fe_2O_3 \cdot nH_2O$ which is a slimy dark-brown semi-suspended material. This process often takes place in the standing water in the borehole. Thus, to collect a representative water sample, the borehole must be properly purged and the water sample filtered.

Manganese and iron in groundwater behave similarly and thus the sampling procedure is the same. Mn(II) oxidises to Mn (IV).

The sample container can be glass or plastic. The laboratory procedure involves acidifying the water sample to dissolve the iron and manganese. Thus it is very important to ensure that there is no iron or manganese precipitated on the inside of bottles used previously. Thus use either new bottles or preferably acid-washed bottles which are prepared in the laboratory before going into the field. Filter the sample immediately it is discharged. No preservative is needed, but keep it cool.

4.2.5 TRACE AND HEAVY METALS

Which of the many trace and heavy metals to analyse the water sample for depends on what information is required from the groundwater monitoring programme.

Generally the trace and heavy metals are relatively immobile under normal groundwater flow conditions. When low pH and/or Eh occurs as is typical at a pollution site, the trace metal concentrations can become a critical factor, as under these conditions the metals may be in the soluble phase and are thus mobile. When the groundwater is brought to surface, CO_2 degassing and exposure to the atmosphere occurs, the pH rises, the Eh tends towards oxidising conditions and the valence state of some of these metals can change, causing them to precipitate onto the sample bottle. In addition, when iron or manganese precipitate, they are strong scavengers (adsorption) and will change the concentration of many metals in solution

(co-precipitation). It is thus very important to collect a filtered sample for analysis. The filtration must take place as rapidly as possible after the groundwater has been brought to surface and with minimum exposure to the atmosphere. This filtered water must be immediately acidified to pH < 2 to prevent the metals from precipitating.

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 water 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.

When a water sample is not filtered, suspended solids are collected as well. If this water sample is acidified and analysed for metals the results merely represent 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. Total metals is thus a meaningless parameter for interpreting groundwater quality. 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 is also 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. Even better 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.

Hexavalent chromium is toxic. To analyse groundwater for Cr^{6+} is expensive and the holding-time (< 24 hrs) 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.

4.2.6 RADIOACTIVITY

This covers amongst others, radon (Rn-222), radium (Ra-226), uranium, iodine (I-131) and strontium (Sr-90) if contamination is suspected and various other elements if age-dating is to be carried out. If you plan or are considering carrying out such a monitoring programme consult the analytical laboratory for containers, preservation and reagents. In particular, reference should be made to procedures specified by the Council for Nuclear Safety (CNS) for sampling of water containing uranium and/or thorium and their decay products. The filter type, the filter pore size, and the two filtration steps are specified (CNS, 1990).

Note that polyethylene bottles are preferred as glass containers have a higher background radioactivity than polyethylene. Whichever container is selected must be tested for background radioactivity. The bottles should be acid-washed. The preservative used is highly dependent on the radiochemical to be analysed and should be tested for radioactivity prior to use.

Similar to metals radioactive elements will precipitate or adsorb onto iron. Thus the water sample must be filtered as quickly as possible. The exception is radon which is a dissolved gas.

The sampling method for radon must be one that reduces degassing (see petroleum-derived compounds, Section 4.3.3.4). The sample container for radon must be one that can be filled so that there are no air-bubbles and should be similar to those used for VOC's. For radon do not filter the water sample as this encourages degassing and loss of radon.

4.3 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 humid acids. DOC (dissolved organic carbon) analyses show the common range to be 0,1-10 mg/L.

DOC is a relatively cheap parameter 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 encountered in groundwater COD is meaninglessly inaccurate and should not be used unless serious contamination is known to occur. COD analyses are twice the price of DOC, or more, depending on the laboratory.

It is in the field of man-made organic compounds and their impact on groundwater that is of increasing concern from a water quality viewpoint. It is here that the parameter Total Organic Halogen or TOX is an important measurement. This is a field in which many questions are only partially answered or even unanswered. Extensive work is being carried out especially in the USA, to develop analytical techniques,

to refine sampling methodology, to understand the subsurface behaviour of these organic compounds and to understand their effect on groundwater consumers, to name a few. The 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 entitled *Toxicological Risk Assessment* (Lehr, 1989).

"The number of identified man-made organic compounds now totals near 2 million and is growing at a rate of about 250 000 new formulations annually, of which 300-500 reach commercial production (Giger and Roberts, 1977). More than 1200 individual man-made organic substances have been identified in drinking water supplies (Shackelford and Keith, 1976). 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 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:

- phenols
- trihalomethanes
- pesticides
- petroleum-derived compounds

General groups:

- dissolved organic carbon (DOC)
- dissolved organic halogen (DOX)
- volatile organic compounds (VOC)
- semi-volatile (or non-volatile) organic compounds (NVOC)
- 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 quantify individual organic compounds; and
2. Those that quantify the total amount of organic compounds which have a common characteristic.

4.3.1 SAMPLE CONTAINERS

Many of the organic compounds are toxic or pose a threat at very low concentrations. For some specific organic compounds in the USA the drinking water standards are in the 0,0001 to 0,01 mg/L range. Consequently, bias by cross-contamination is of particular concern and special care must be taken with the sample containers.

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 sample volume needed varies from 25 mL to 2 L. Examples of two-litre bottles which can be used are empty "Winchester" bottles previously used for reagents and obtainable from the analytical laboratory. Some laboratories prefer wide-mouthed bottles so that a stirrer can be inserted into the bottle. The stirrer thoroughly mixes the extractant with the water.

The cap should be inert metal lined with Teflon. Teflon liners are often difficult to obtain so a useful 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 cleaned prior to sample collection. The accepted cleaning procedure is to wash in hot detergent solution, rinse in warm tap water, rinse in dilute hydrochloride acid, and finally rinse in distilled water. The bottles are then put into an oven at 300 °C overnight. The Teflon cap liners and metal caps are washed in detergent. The caps are rinsed with distilled water and air dried. The liners are rinsed in dilute hydrochloric acid, soaked in redistilled acetone for several hours, and heated to 200 °C overnight. When the heat treatments are completed, the bottles are capped with the closure and Teflon liners.

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

4.3.2 SAMPLING EQUIPMENT

The sampling device that is 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 MCL (Maximum Contaminant Level, USA Regulations) 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 must 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, centrifugal pumps (which include electric submersibles) and air-lift pumps. Gas-driven piston pumps have limited suitability for volatile organic sampling. 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 organics or sinking organics. In either case use a clear-wall bailer so that you can measure the thickness of the organics. Other than in these two specific cases bailers have limited suitability.

The method of choice and the ONLY recommended pump is a bladder pump, preferably of all-Teflon construction.

Refer to Chapter 10 where sampling devices are discussed in more detail.

4.3.3 MORE COMMONLY ENCOUNTERED ORGANIC CONTAMINANTS

4.3.3.1 PHENOLS

Phenols are hydroxy-derivatives of benzene, including halogenated hydroxy-benzenes. The empirical formula for phenol is C_6H_6O and halogens (Cl, F, Br) and other functional groups can substitute for H on the benzene ring.

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.

Unfiltered water samples are collected in properly cleaned 1 L glass bottles. Analytical grade H_2SO_4 is added to achieve a $pH < 2$. Samples are kept cool, and must be analysed within 28 days. Phenols are semi-volatile so you do not need to fill the bottle completely.

4.3.3.2 TRIHALOMETHANES (THMs)

THMs are found in most chlorinated water supplies and are typically produced in the treatment process as a result of chlorination. These compounds have been shown to form when organic acids (e.g. fulvic acid, humid acid), algae (green, blue-green and diatom algae) and other soluble, low-molecular weight organic compounds (phenolic compounds) are exposed to chlorine and bromine. Chlorine is available during chlorination, but the source of bromine has not yet been clearly established.

The THMs commonly found in drinking water are:
trichloromethane (chloroform) ($CHCl_3$),
dichlorobromomethane ($CHCl_2Br$),
dibromochloromethane ($CHClBr_2$) and
tribromomethane (bromoform) ($CHBr_3$).

Less common are:
methylene chloride (CH_2Cl_2),
methylene bromide (CH_2Br_2),
ethylene chloride ($C_2H_2Cl_2$) and
carbon tetrachloride (CCl_4).

Total trihalomethanes (TTHMs) are defined as the arithmetic sum of the concentrations of trichloromethane (chloroform), dibromochloromethane, dichlorobromomethane and tribromomethane (bromoform). The standard method of analysis is applicable only to these four.

The cause for concern over the concentration of TTHMs is that elevated values may be harmful to human health. Toxicological studies suggest that chloroform and bromoform are potential human carcinogens.

Sample bottles must be properly cleaned glass bottles sealed with a Teflon seal and NO head-space i.e. after sampling no air-bubbles should be present as TTHMs are volatile and will be lost if head-space is present. Either 25 mL brown glass or clear glass bottles stored in light-free containers should be used. The preferred cap is a screw cap with a hole in the centre and which is sealed with Teflon.

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. For each sample point you must collect two samples (one plus a duplicate).

Sample preservation depends on what information is needed. The normal set to collect comprises:

1 raw water before chlorination
2 water from the post-chlorination stream.

Raw-water before chlorination. Collect two samples with no preservative and two samples with excess free Cl_2 added (1 drop of household bleach per 25 mL). The latter two samples are for testing TTHM formation potential.

Water from the post-chlorination stream. Collect two samples with no preservatives and two samples with L(+)ascorbic acid added (½ saltspoon per 25 mL) which neutralises any free chlorine and thus prevents further formation of TTHMs after the sample has been collected. All samples must be kept cool.

Before going into the field to collect the sample, know what you want to investigate and consult the analytical laboratory.

4.3.3.3 PESTICIDES

Pesticides include insecticides, herbicides, fungicides, nematicides and molluscicides. They vary widely in toxicity to humans so that for some pesticides a few grams is 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 need not be swallowed to be dangerous. 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 and others carcinogenic.

The EPA's National Pesticide Survey (NPS) has identified six analytical methods which in total analyse for 100 pesticides and their degradation products (Munch *et al.*, 1990). The method, the pesticide type, the volume of water needed and the preservation method are detailed in Table 4.3.3.3.

Table 4.3.3.3 Pesticides: Sample volume, extractant and preservative requirements (Munch *et al.*, 1990)

NPS Method No	Pesticide type	Volume of sample mL	Extractant	Preservative
1	Nitrogen phosphorous containing pesticides	1000	dichloromethane	cool
2	Chlorinated pesticides	1000	dichloromethane	cool
3	Chlorinated acids	1000	dichloromethane	cool
4	Pesticides using High Performance Liquid Chromatography	1000	dichloromethane	cool
5	N-methyl carbamoyloximes and N-methyl carbamates	25	-	cool
6	Ethylene thiourea (ETU)	50	-	cool

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. Pesticides can be degraded by microbiological activity, so to inhibit biodegradation keep the sample cool. 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 these preservation methods in addition to keeping the sample cool.

4.3.3.4 PETROLEUM-DERIVED COMPOUNDS

These include the various petrol compounds, paraffins and specifically benzene, toluene, xylene and methyl t-butyl ether (MTBE). These latter four have been identified by the EPA as priority pollutants (Gillham *et al.*, 1983).

These compounds pollute groundwater where underground storage tanks (UST) start leaking, typically at a garage selling petrol and also when tank farms have spillages or leaks.

These compounds are volatile so the sampling pump must be a bladder pump. A clear-sided bailer is useful to measure the thickness of floating organic compounds in the borehole BEFORE purging takes place.

Use properly cleaned 50 mL glass bottles fitted with a screw cap which has a hole in the centre. Use Teflon cap-liners. The hole in the centre is so that the bottle does not have to be opened with consequent loss of volatiles compounds. The Teflon is merely pierced and the sample removed. For each sampling point collect two samples (one plus a duplicate). Keep cool at 4 °C to reduce biodegradation.

4.3.4 GENERAL GROUPS OF ORGANIC COMPOUNDS

4.3.4.1 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 undissolved or particulate organic carbon. The DOC in turn comprises the volatile and the non-volatile fractions.

Most determination methods involve purging the inorganic carbon (dissolved CO_2 and CO_2 produced by acidifying the sample to convert bicarbonate to CO_2) plus the volatile organic carbon fraction (VOC) with nitrogen gas. This is followed by chemical or thermal oxidation of the non-volatile organic carbon to CO_2 and measuring this CO_2. VOC can be determined by trapping the VOC during the initial purging steps. However this is seldom done as DOC is intended as a screening method at low cost and this step will add significantly to the cost and also needs different field-sample collection techniques.

The concentration range of DOC in most groundwaters is typically 0,5 to 10 mg/L and is composed primarily of fulvic and humid 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 can 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 (Chapter 4.2.1).

If the VOC content is needed then follow the procedure outlined under Volatile Organic Carbon, section 4.3.4.3.

4.3.4.2 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 trichloroethene, tetrachloroethene, and other halogenated alkanes and alkenes; chlorinated and brominated pesticides and herbicides; polychlorinated biphenyls (PCBs); chlorinated aromatics such as hexachlorobenzene 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. The possibility of overestimating DOX concentration because of inorganic halide interference always should be considered when interpreting results" (APHA, 1989).

CHAPTER 11 - SAMPLE COLLECTING DEVICES

CHAPTER 12 - PURGING THE BOREHOLE

CHAPTER 13 - FILTERING DEVICES

CHAPTER 14 - FLOW-THROUGH CELL

CHAPTER 15 - MULTIPLE LEVEL SAMPLING

CHAPTER 16 - PROTECTIVE CLOTHING

CHAPTER 17 - DECONTAMINATION

The DOX spectrum comprises both volatile and non-volatile components. The DOX analytical method measures these 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 airstripping 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 acid and keep cool at 4 °C. Samples should be analysed within 14 days.

If you are sampling a post-chlorination stream then reduce the residual chlorine by adding a small pinch of sodium sulphite crystals (20 mg/L).

As volatiles are part of DOX the only suitable sampling pump is a bladder pump. A syringe is suitable but cannot be used for purging. As volatiles are part of DOX the sample must NOT be filtered as this will cause loss of volatile compounds.

4.3.4.3 VOLATILE ORGANIC CARBON (VOC)

THMs and petroleum-derived compounds as described in section 4.3.3.2 and 4.3.3.4 are included in this group. Please read these chapters before continuing. Other compounds falling into this category are solvents and degreasers. Follow the sampling methodology as described under section 4.3.3.4 "Petroleum- derived compounds". 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 °C.

This group is also referred to as "Purgeable Organic Compounds" 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.

4.3.4.4 SEMI-VOLATILE ORGANIC COMPOUNDS

Pesticides, as described in section 4.3.3.3, are included in this group. Other compounds include fuel oils, dye residues, wood preservatives, plasticisers, coal tar, PCBs and other priority pollutants.

These organic compounds are also known as either acid-extractable organic compounds or base/neutral-extractable organic compounds.

The sampling device recommended is a bladder pump, however there is less danger of volatilization so that a submersible centrifugal pump can be used if a bladder 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 °C.

4.3.4.5 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, such as chloroform, CFCs and dichloromethane.

Note that DNAPLs can move faster than groundwater.

These two classes of organic compounds will always be pollution site 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 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 screwcap. Drop the bailer to the bottom of the borehole and collect the DNAPL sample, measure the thickness, 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.

4.4 MICROBIOLOGICAL DETERMINANDS

4.4.1 INTRODUCTION

The SABS (1984) specification No 241 specifies recommended and maximum allowable limits for the following bacteriological requirements:

- Standard plate count
- Total coliforms
- Faecal coliforms

Criteria proposed for South Africa drinking water (Pieterse, 1989) add 3 further determinands, namely:

- *Clostridium perfringens*
- Coliphages
- Enteric viruses

The recommended limits for the above six are detailed in Chapter 19. In South Africa there are no legally enforceable drinking water standards. However, the Department of National Health and Population Development is considering the introduction (and has already accepted the basic philosophy) of certain drinking water quality guidelines based on recommendations by the CSIR (Pieterse, 1989).

The subsurface environment, both in the vadose zone and the saturated zone, has a huge 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 *Streptococcus faecalis* (indicator of recent faecal pollution for which survival rates are higher than for faecal coliforms) and to the mostly nameless species of bacteria which mineralise organic carbon. It is in this latter sphere of activity that extensive and on-going research is being conducted, especially in the U.S.A.

In the sphere of groundwater pollution interest in micro-organisms is particularly high. Micro-organisms 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 input 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, some companies are already selling bacteriological clean-up expertise.

What is briefly discussed above is a vast field and involves fairly specialized collection, transport and analytical techniques. As these techniques would require a manual on its own as well as rapid updating, only the six micro-organisms named at the start of this chapter are discussed below.

4.4.2 S.A. MICROBIOLOGICAL DETERMINANDS

4.4.2.1 HETEROTROPHIC PLATE COUNT

The test (previously known as the standard 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 35-37 °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. It is useful 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 aftergrowth or secondary contamination in distribution systems.

4.4.2.2 TOTAL COLIFORMS

This gives an indication of the sanitary quality of water. The coliforms originate from man, animal, plants and the environment and consist mainly of *Escherichia coli (E.coli)*, species of *Klebsiella, Citrobacter. Enterobacter* and *Aeromonas hydrophila*. This includes all bacteria which produce a colony with a golden green metallic sheen within 18-24 hours of incubation at 37 °C on mFC Endo Agar Les.

4.4.2.3 FAECAL COLIFORMS

This gives an indication of probable faecal pollution and is much more closely associated with faecal pollution than total coliforms, although some may not be of faecal origin. They consist mainly of *E.coli* but may also include *Klebsiella, Citrobacter* and *Enterobacter*. This includes all bacteria which produce a blue colony on mFC Agar within 18 to 24 hours of incubation at 44,5 °C. *E.coli* predominates among the aerobic organisms present in the healthy gut.

4.4.2.4 CLOSTRIDIUM PERFRINGENS

There are 5 types designated A to E distinguished by the various toxins they produce. This is the organism most commonly associated with gas gangrene. *Clostridium perfringens* is a primary faecal and pathogenic organism. *Clostridium perfringens* can live longer in the natural environment than *E.coli*. As such its main use as an indicator organism is that the presence of *Clostridium perfringens* and the absence of *E.coli* indicates either remote faecal pollution or previously occurring faecal pollution.

It is an obligatory anaerobic spore-forming gram-positive bacilli. The spores are exceptionally resistant to unfavourable environmental conditions and water treatment processes. The spores also resist the action of the routinely used antiseptics and disinfectants. The spores of the food-poisoning strains are markedly heat-resistant and may survive boiling for several hours.

4.4.2.5 COLIPHAGES

E.coli is the host bacterium for this group of bacteriophages. The survival rate of a coliphage is higher than that of all the indicator bacteria (faecal coliforms including *E.coli*). Therefore the presence of coliphage combined with the absence of *E.coli* indicates that *E.coli* was present but either has died-off or the pollution source is distant.

4.4.2.6 ENTERIC VIRUSES

These are viruses which multiply in the gastro-intestinal tract of warm-blooded animals and include entero-, Coxsackie, reo-, adeno- and rotaviruses as well as the hepatitis A and Norwalk viruses.

These viruses can survive for some time in nature and diseases can be transmitted via water. Polio, echo and Coxsackie B are reported as "enteroviruses". The viruses of major concern in health aspects are the Coxsackie A, adeno-, hepatitis A, rota- and Norwalk viruses.

4.4.3 SAMPLE CONTAINERS FOR MICRO-ORGANISMS

These can be glass or plastic but must be made of a material that can be sterilized at 121 °C for 15 minutes in an autoclave or in an oven at 170 °C for 120 minutes. The seal/cap must be able to close so that contamination cannot occur after sterilization.

The sampler will contact the laboratory who will supply the sterile bottles which are needed. Again plastic is preferred to glass as plastic is less prone to breakage.

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.

4.4.4 COLLECTING, PRESERVING AND HANDLING OF GROUNDWATER MICROBIOLOGICAL SAMPLES

Purge the borehole properly. Use a sample collecting device as stated on page 11-3. Do NOT filter the water.

When collecting the water sample, 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. Be very careful not to touch the inside of the cap or the bottle. Record the time and date of sampling on the bottle. Store the filled bottles on ice (4 °C) and in darkness. The sample should be analysed within 6 hours and the maximum recommended holding time is 24 hours.

The matrix of Table 4.4.1 shows the sample size, holding time and incubation times of the various determinands.

Table 4.4.1 Micro-organism sample size requirement and holding time

Determinand	Sample Volume	Recommended Holding Time	Maximum Holding Time	Incubation Period
- Heterotrophic Plate count				48 hours
- Total coliforms		Up to		24 - 48 hours
- Faecal coliforms	Total 1 L	6 hours	24 hours	22 hours
- *Clostridium perfringens*				18 hours
- Coliphages				8 - 24 hours
- Enteric viruses	12 L or more	Up to 6 hours	18 hours	2 - 4 weeks

4.4.5 PROBLEM AREAS

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.

If you are collecting water from a reticulation system as part of your programme determine whether the water is chlorinated. If so, neutralize the free chlorine by adding 1 mL of 30 % (m/v) sodium thiosulphate per 1 L of sample.

4.5 REFERENCES

APHA 1989 Standard Methods for the examination of water and wastewater. 17th Edition. Washington, D.C., Am. Public Health Assoc.

Council for Nuclear Safety 1990 Licensing guide to safety assessment at mines and works, Appendix 2. P O Box 7106, Hennopsmeer, 0046, South Africa.

Everett, G.L. 1980 Groundwater monitoring. Genium Publishing Corporation. Schenectady.

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.

Giger, W. and P.V. Roberts 1977 Characterization of refractory organic carbon. Water Pollution Microbiology, 2, ed. Ralph Mitchell, Wiley-Interscience, New York.

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

Munch, D.J., R.L. Graves, R.A. Maxey and T.M. Engel 1990 Methods development and implementation for the National Pesticide Survey. Environ. Sci. Technol., 24, (10).

Pieterse, M.J 1989 Drinking-water quality criteria with special reference to the South African experience. Water S.A. 15 (3), Water Research Commission, Pretoria.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby and J. Fryberger 1981 Manual of ground-water sampling procedures. National water well association. Worthington, Ohio.

Shackelford, W.M. and L.H. Keith 1976 Frequency of organic compounds identified in water. Analytical Chemistry Branch, Environmental Research laboratory, Athens, Ga.

CHAPTER 5

FIELD DETERMINANDS

Field determinands are collected for two reasons, namely:

- to check purge volumes (see Chapter 12)
- to measure unstable determinands.

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

They must consequently be measured at the borehole 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.

To check purge volumes, pH and EC are measured on a continuous basis. If these two determinands are stable for the duration of purging of one well volume then sample collection can start.

Temperature affects many chemical and biological rates. Temperature is the easiest of all field measurements to take.

Electrical conductivity is a function of the activities of ionic species in solution. Thus physical or chemical changes caused by exposure of the groundwater sample to the atmosphere will affect it.

When groundwater is brought to surface, degassing occurs, particularly of CO_2. This will cause an increase of pH of up to 2,5 pH units. A knowledge of the *in situ* pH is essential to reconstruct the potential mobility of constituents.

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 and precipitation of constituents can occur. 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. Thus DO needs to be measured using a *flow-through cell*. DO measurement is essential for groundwater pollution studies as the DO concentration regulates the valence state of trace metals and constrains the bacteriological metabolism of organic compounds.

Alkalinity is measured in the field as 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.

5.1 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. It is important to measure temperature at the same time as EC is being measured because EC is affected by temperature (I will discuss this relationship further in the following section). Species solubility is temperature controlled i.e. for most species the higher the temperature the more soluble they are. The exception is calcium which is the reverse, which is why scale is deposited on the inside of your kettle.

The major factor controlling corrosion is CO_2 solubility which is temperature dependent. Thus to estimate the dissolution potential of a groundwater, you must measure temperature and pH accurately.

5.1.1 EQUIPMENT

Two mercury thermometers that can be read to 0,2 °C and that have been calibrated (one is a spare as they are prone to breakage) or a digital thermometer. These are generally accurate and are often incorporated in pH meters.

5.1.2 FIELD METHODS

1. Rinse the thermometer with reagent grade water.
2. Immerse the thermometer in the sample.
3. Wait for the temperature to equilibrate.
4. Read and record the temperature to the nearest 0,5 °C while the thermometer is immersed in the water (do not pull the thermometer out and read it while it's in the air).
5. Rinse the thermometer with reagent grade 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 as the water will have been heated/cooled.

5.2 ELECTRICAL CONDUCTIVITY- EC

5.2.1 INTRODUCTION

Conductivity is the ability of an aqueous solution to conduct an electric current. ASTM (1969) defined the electric conductivity of water as the "reciprocal of the resistance in ohms measured between faces of a centimetre cube of an aqueous solution at a specified temperature."

This ability 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 conduct a current very poorly, if at all (APHA, 1989).

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, reports conductivity in millisiemens per metre (mS/m). In the USA the unit of measurement is micromhos per centimetre (mhos/cm). Some instruments have various scales of sensitivity and unfortunately have named these scales in various fashions such as millisiemens per centimetre or microsiemens per centimetre. All measurements *must* be reported in mS/m.

Conversion table for units used to record EC

1 Siemen per cm	x	1000	= 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 Purging the borehole, page 12-1).

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; therefore, it is essential to obtain an accurate field determination". (Wood, 1981)

5.2.2 EC AND TDS (TOTAL DISSOLVED SOLIDS)

"TDS is a measure of the 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 of heating.

Residues dried at 103 to 105 °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 $\pm$2 °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 °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, 1989)

To ask for TDS measurement by drying and weighing by a laboratory is time-consuming and thus 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 x EC. The factor A is between 5,5 and 7,5 with the most commonly used conversion factor being 6,4. Of course, if a full analysis of the major and minor constituents is made then TDS can be calculated by summation of the ions.

5.2.3 METHOD

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 °C (Wood, 1981). The standard temperature for reporting EC is 25 °C. Thus you must measure the temperature accurately in order to obtain an accurate EC. Modern

conductivity meters have temperature compensators and thus the EC can be read directly as mS/m at 25 °C. 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 and alter the cell constant. If this happens immerse the cell in dilute HCl to clean.

Other materials that may precipitate or foul the electrode are Fe and organic compounds.

5.2.4 APPARATUS

(1) EC meter
(2) EC electrode
(3) Thermometer graduated in 0,2 °C
(4) 1000 mL plastic beaker
(5) Flow-through cell (optional)

5.2.5 FIELD PROCEDURE

(1) Read the manufacturer's instructions for specific procedures for the instrument.
(2) Calibrate the instrument, either in the field or in the laboratory before leaving for the field, with a standard EC water. **Note:** make sure the EC meter you purchase can be calibrated, otherwise it is a waste of money.
(3) Start pumping the borehole.
(4) Measure the water temperature.
(5) 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.
(7) Take the reading, make sure it is in mS/m and record.
(8) Rinse the cell with distilled water and pack away wet.

Note: Possible errors in reading can be made if the electrode is either not fully immersed or air bubbles are on the platinum electrodes.

5.2.6 REFERENCES

American Society for Testing Materials 1969 Manual on Water, ASTM Special Technical Publication, (442).

APHA 1989 Standard Methods for the examination of water and wastewater. 17th Edition Washington, D.C., Am. Public Health Assoc.

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.

5.3 pH

5.3.1 INTRODUCTION

pH is a measurement of the concentration of hydrogen ions in solution. 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 and degassing of a sample can significantly alter its pH. For example, during a water sampling project, I observed that CO_2 degassing from low TDS groundwater from Table Mountain quartzite caused the measured pH to change from 4,9 to 7,1. In practical terms a 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 metal species. The Eh-pH phase diagrams should be well known to all hydrogeologists. To be able to determine whether or not a metal is soluble and thus mobile in groundwater you must determine what the *in situ* pH and Eh are. Thus you must measure pH in the discharge stream as close to the borehole as possible. If you are measuring DO and/or Eh as well and are thus using a flow-through cell (Chapter 14) then also use the flow-through cell for the pH electrode. Although use of a flow-through cell is recommended for pH measurement, it is not essential.

5.3.2 METHOD OF pH MEASUREMENT

pH is determined with a glass electrode compared with a reference electrode of known potential by means of a pH meter or other potential measuring device with a very high input impedance (Wood, 1981). The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by interpolation.

The glass electrode is relatively free from interference from colour, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at pH > 10. pH measurements are affected by temperature in two ways (1) mechanical effects that are caused by changes in the properties of the electrodes and (2) chemical effects caused by equilibrium changes. For precise determinations, the standard buffers should be within ± 1 °C of the sample solution (APHA, 1989).

5.3.3 pH MEASURING APPARATUS

5.3.3.1 pH METER (from APHA, 1989)

A pH meter consists of a potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test

solution. Many pH meters are capable of reading pH and millivolts. The millivolt scale is an important feature as this same meter using a different electrode is used for measuring Eh in mV.

For routine work, use a pH meter accurate and reproducible to 0.1 pH unit with a range of 3 to 10 and equipped with a temperature-compensation adjustment.

Although manufacturers provide operating instructions, the use of different descriptive terms may be confusing. For most instruments, there are two controls: (1) intercept (set buffer, asymmetry, standardize) and (2) slope (temperature, offset) - their functions are shown diagrammatically in Figures 5.3.1 and 5.3.2. The intercept control shifts the response curve laterally to pass through the isopotential point with no change in slope. This permits bringing the instrument on scale (0 mV) with a pH 7 buffer that has no change in potential with temperature.

The slope control rotates the emf/pH slope about the isopotential point (0 mV/pH 7). To adjust the slope for temperature without disturbing the intercept, select a buffer that brackets the sample with pH 7 buffer and adjust the slope control to pH of this buffer. For example the pH of groundwater from quartzites is usually between 5 and 6, so select buffers pH 4 and pH 7 to calibrate the meter.

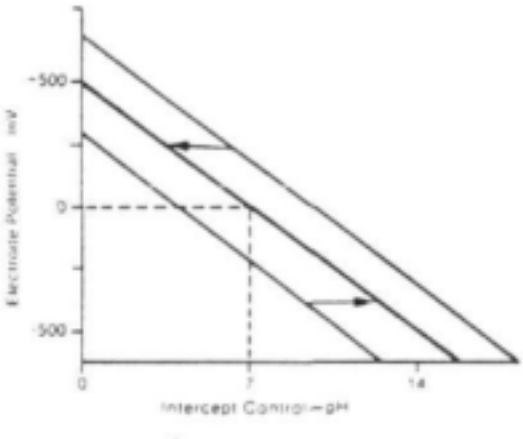

Figure 5.3.1 Electrode potential vs. pH intercept control shifts reponse curve laterally (APHA, 1989)

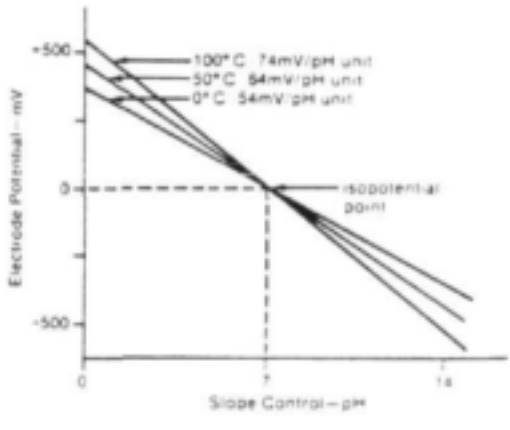

Figure 5.3.2 Typical pH electrode response as a function of temperature (APHA, 1989)

5.3.3.2 THE COLOUR WHEEL

An alternate method to the electronic method of measuring pH is to use a pH colour indicator such as bromo-thymol blue which has different shades of blue for pH values between 6 and 7.5. This is matched with a colour wheel

and the corresponding pH recorded. This method has a number of shortcomings the main being its low level of sensitivity. The indicator and the colour wheel are also prone to colour changes caused by UV light and heat.

5.3.3.3 ELECTRODES

Two electrodes are needed to measure pH:

(1) *reference electrode* consisting of a half-cell that provides a constant electrode potential;

(2) A *glass electrode* which is a bulb of special glass containing a fixed concentration of KCl or a buffered chloride solution in contact with an internal reference electrode.

For general field use, a *combination electrode* is recommended as it is much easier to handle a single electrode than two electrodes. The combination electrode incorporates the *glass electrode* and *reference electrode* into a single probe. It is also recommended that an electrode that uses saturated KCl solution (i.e. if crystals are present the filling solution is saturated) is used.

5.3.3.4 EQUIPMENT CHECKLIST

(1) pH meter (make sure the pH meter you purchase has millivolt reading capability so that you can measure Eh)
(2) pH combination electrode
(3) Buffer solutions of pH 4, pH 7 and pH 10 (500 mL each)
(4) 100 mL glass or plastic (use plastic if pH electrode is glass in order to reduce breakage) bottles to hold buffer solution when calibrating the pH meter
(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
(8) Distilled water plus squeeze wash bottle
(9) Table to work on
(10) Flow-through cell (Chapter 14), desirable, but not essential

5.3.3.5 FIELD PROCEDURE FOR pH MEASUREMENT

Ensure electrode is filled with saturated KCl. If low, replenish with warm saturated KCl. Check batteries for leakage every two months. Read the manufacturer's instructions for your specific instrument.

Calibrate the pH meter and measure pH as follows:

(1) Place containers of pH 4 and pH 7 buffer in a bucket with running groundwater for 5 minutes to equalise temperature. If alkaline water is expected, use pH 7 and pH 10 buffers.
(2) Measure the temperature of the running water with a thermometer and set this temperature on the pH meter.
(3) Rinse the pH electrode with de-ionised water and blot dry.
(4) Rinse the outside of the pH 7 buffer bottle, open and immerse pH electrode.
(5) Set pH at 7 with *set buffer* knob (this is intercept adjustment).
(6) Rinse the electrode and blot dry.
(7) Rinse the outside of the pH 4 buffer bottle, open and immerse the pH electrode.
(8) Set pH at 4 with *temperature* knob. (This is slope adjustment).
(9) Rinse electrode, blot dry and re-check value of pH 7 buffer. If the value is within $\pm$0,05 pH of original, proceed with step 10. If drift has occurred, repeat steps 4 to 9.
(10) Rinse electrode, measure pH of a freshly collected sample of groundwater and record.
(11) Rinse electrode and switch off.
(12) For subsequent measurements during the day, rinse electrode, check calibration with pH 7 buffer, measure and record field pH, switch off. Check with pH 4 buffer at intervals during the day.

5.3.3.6 TROUBLE-SHOOTING

- Do not let the electrode dry out, cover with rubber sleeve supplied with the electrode.
- Ensure the glass electrode is filled with solution.
- If a KCl solution is used, ensure it is saturated by checking that crystals are present both in the bulb and the main body of the electrode.
- Ensure electrode is clean. If not, clean electrode by alternately immersing it three times each in 0,1*N* NaOH and 0,1*N* HCl.
- For further trouble-shooting, read Standard Methods 4 500-H$^+$.

5.3.4 REFERENCES

APHA 1989 Method 4 500-H$^+$. Standard methods for the examination of water and wastewater, 17th Edition Washington, D.C., Am. Public Health Assoc.

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

5.4 Eh (OXIDATION-REDUCTION POTENTIAL OR REDOX POTENTIAL)

5.4.1 INTRODUCTION

"Many reactions in groundwater involve the transfer of electrons between dissolved, gaseous and solid constituents. Electron loss results in oxidation and electron gain results in reduction, but since free electrons do not exist in solution, oxidation and reduction occur simultaneously and the overall process is called a redox reaction.

The most important oxidizing agents in groundwater are dissolved oxygen, oxo-anions such as nitrate and sulphate, and water itself. Reducing agents in groundwater include a wide variety of organic compounds such as carbohydrates, humic substances, and hydrocarbons, inorganic sulphides such as pyrite, and iron(II) silicates. Most aquifers contain at least one of these groups of reducing agents, while most water entering aquifers contains oxidizing agents such as dissolved oxygen and nitrate.

As groundwater passes through an aquifer, oxidizing agents in the water are consumed progressively by reaction with reducing agents in the aquifer, the most powerful oxidizing agents reacting first. Dissolved oxygen is the most powerful oxidizing agent encountered naturally and this is normally consumed within a short distance from the recharge area. Nitrate reduction follows the consumption of oxygen and this may in turn be followed by sulphate reduction. As a corollary, the presence of oxidizing species may indicate recent groundwater recharge". (Lloyd and Heathcote, 1985)

The five progressive evolutionary phases of groundwater through the sequence of the redox process are:

Denitrification
Manganese reduction
Iron reduction
Sulphate reduction
Methane fermentation.

Many of the important redox reactions that occur in groundwater are catalysed by bacteria and other micro-organisms. The sequence of redox reactions is paralleled by an ecological succession of micro-organisms, with various bacterial species adapted to the different stages of the redox condition.

"Aqueous solutions do not contain free electrons, but it is nevertheless convenient to express redox processes as half-reactions and then manipulate the half-reactions as if they occur as separate processes. Within this framework a parameter known as

the pE is used to describe the relative electron activity. By definition,

$$pE = -\log [e]$$

pE, which is a dimensionless quantity, is analogous to the pH expression for proton (hydrogen-ion) activity. The pE of a solution is a measure of the oxidizing or reducing tendency of the solution. In parallel to the convention of arbitrarily assigning $G^\circ = 0$ for the hydration of H^+ (i.e., $K_{H+} = 0$ for the reaction $H^+ + H_2O = H_3O^+$) the free-energy change for the reduction of H^+ to $H_2(g)[H^+ + e = \frac{1}{2}H_2(g)]$ is zero. pE and pH are functions of the free energy involved in the transfer of 1 mol of electrons or protons respectively". (Freeze and Cherry, 1979)

The redox potential can be expressed in terms of:

- pE (dimensionless)
- Eh (volts or preferably millivolts)
- G (joules or calories).

Eh has been used in many investigations although pE is becoming more popular. Eh is referred to as redox potential. Eh and pE are related by the equation

$$pE = \frac{nF}{2.3\,RT}\,Eh$$

where F is the faraday constant (9.65 x 10^4 C/mol), R the gas constant, T the absolute temperature, and n the number of electrons in the half-reaction.

The redox potential of groundwater can be measured directly by measuring the electrical potential in the water using an electrode system which incorporates an inert metallic electrode, usually platinum. These are called Eh probes and they are used with pH meters. This method is qualitative but is a valuable tool for understanding groundwater systems and especially so for groundwater pollution investigations.

For detailed discussions of the theory and significance of the electrode approach to redox measurement read Hostettler (1984), Lindberg and Runnells (1984), Stumm and Morgan (1981), Thorstenson (1971), Whitfield (1974).

5.4.1.1 DO AND Eh

If the groundwater sample has DO (dissolved oxygen) then the Eh can be calculated using the formula:

$$pE = 20.78 + \tfrac{1}{4}\log(P_{O_2}) - pH$$

where P_{O_2} is the partial pressure of O_2 and is calculated from the DO measurement and Henry's Law.

$$P_{O_2} = \frac{O_2 \text{ dissolved}}{\sqrt{K_{O_2}}}$$

where K_{O_2} at 25 °C is $1{,}28 \times 10^{-3}$ mol/kPa.

At the detection limit of field DO meters, which is 0,01 mg/L, the calculated pE of water at pH 7 is 13,1, or expressed as Eh, +780 mV. Water saturated with oxygen at pH 7 has a pE of 13,6. If the DO is close to or below detection limits calculating Eh from DO is not possible and you must measure the Eh using an Eh probe and a pH meter which has millivolts reading capabilities.

5.4.2 MEASUREMENT OF Eh

Eh is measured with a noble metal (usually platinum) electrode and a reference electrode system using a pH meter that can be read in millivolts. Reference solutions with known Eh are used to obtain the potential and to check the accuracy of the electrode system.

Generally the description in groundwater sampling manuals of how to measure Eh is inadequately described. The usual instructions given are "follow the manufacturers instructions" and these are invariably difficult if not impossible to carry out. Thus for the purposes of this manual I have described four methods in detail. These four methods have as the constant the electrode with the variables being

either - one of two standard solutions
or - one of two types of pH meter with millivolts reading capabilities.

5.4.2.1 THE METER

The meter is a pH meter which has the facility to measure millivolts. Some pH meters have a adjusting knob with which the millivolt scale can be adjusted. This is preferred to those pH meters without this facility as by using this knob, you reduce the number of calculations in the field.

The field method will be described using:

1. - a pH meter WITH a millivolts scale zero adjusting knob.
2. - a pH meter WITHOUT a millivolts scale zero adjusting knob.

5.4.2.2 THE ELECTRODE

I have taken the liberty of prescribing the electrode which must be used as being the *CALOMEL ELECTRODE*. If you use any other electrode you must know the potential of your chosen electrode against the standard hydrogen electrode. The calomel electrode comprises a chloride probe enclosed in a glass tube which is filled with saturated KCl solution. Saturation is maintained by the presence of KCl crystals. The end of the glass tube is porous which allows a liquid junction to exist between the electrode and the water which is to be tested. This electrode is used in conjunction with a platinum electrode which is platinum plate or wire fused to a glass tube with through connection to the electrode cable. These two electrodes can be combined into a single combination electrode which is handy for field use, i.e. you only need one access port in your flow-through cell. Eh MUST be measured using a flow-through cell. Two electrodes recommended are:

- Radiometer PK140 (Combined Redox Electrode)
- Orion 96-78-00 (Combined Redox Electrode)

5.4.2.3 THE REFERENCE SOLUTION

Two reference solutions are recommended:
- *Quinhydrone buffer solution*
- *ZoBell solution*

I prefer the quinhydrone buffer solution to ZoBell solution as by using different pH buffers to make the solution you can cover a redox range +700 to +167 mV whereas ZoBell solution has a potential of only +428 mV at 25 °C. As natural and polluted groundwater ranges from +700 to -200 mV the quinhydrone buffer solution is more flexible as the difference between the reference solution and the groundwater is less, which decreases the possible degree of error in measurement of Eh. Furthermore ZoBell solution is poisonous and must be handled with care.

5.4.2.3.1 QUINHYDRONE BUFFER SOLUTION (from Kokholm)

Quinhydrone buffer solution consists of equal parts of hydroquinone and quinhydrone. Hydroquinone is the reduction counterpart of the oxidation agent quinone. Quinhydrone buffer solution is made by adding quinhydrone crystals to a suitable acid-base buffer solution until a state of saturation is reached, i.e. add until no more crystals dissolve and then a few more. The redox potential of this solution is dependent on the solution pH and temperature as follows:

$$Eh = +700 - 0{,}1983.T.pH$$

where T is absolute temperature (T = t °C + 273,15) and pH is the pH of the buffer solution which may only be in range pH 1 - pH 9.

Thus the Eh of quinhydrone in a buffer solution pH 7 at various commonly encountered groundwater temperatures is:

Table 5.4.1 **Variation of the Eh of quinhydrome buffer pH 7 solution due to temperature changes**

Temperature (°C)	Eh of quinhydrone buffer pH 7 solution relative to standard hydrogen electrode (mV)
10	307
15	300
16	298,6
17	297,2
18	295,8
19	294,4
20	293
25	286

The incremental difference is 1,4 mV per °C.

The purpose of knowing the Eh potential of the solution at various temperatures is so that you can immerse the reference solution in flowing groundwater, equalise and measure temperature and then calibrate the pH meter.

5.4.2.3.2 **ZOBELL SOLUTION**

ZoBell solution was named after C.E. ZoBell who in 1946 examined and developed methods for measuring redox potential in marine sediments. ZoBell solution is made by dissolving:
1,4080 g of potassium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$ (0,00333*M*)
1,0975 g of potassium ferricyanide $K_3Fe(CN)_6$ (0,00333*M*)
7,4555 g of potassium chloride KCl (0,10*M*)

in distilled water to make 1 litre. This solution is stable for several months but should be kept in a black plastic bottle and out of sunlight as much as possible. It has a standard potential of +428 millivolts at 25 °C. The solution is poisonous and should be handled with care (Wood, 1981).

The potential of this solution varies with temperature according to the following equation.

Eh = 0,428-0,0022 (t-25) volt giving:

Table 5.4.2 Variation of the Eh of Zobell solution due to temperature changes

Temperature (°C)	Eh of ZoBell solution relative to the standard hydrogen electrode (mV)
10	+461
15	+450
16	+448
17	+446
18	+443
19	+441
20	+439
25	+428

5.4.2.4 **FIELD PROCEDURES - FOUR METHODS**

To summarise the combination of equipment of a choice of two meters, a choice of two solutions and the specified calomel electrode yields a choice of four methods.

All four methods use the calomel electrode with platinum reference	Quinhydrone solution	ZoBell solution
pH meter WITH zero adjustment of millivolt scale	Method 1	Method 2
pH meter WITHOUT millivolt scale adjustment capabilities	Method 3	Method 4

Method 1

(1) Meter with millivolt scale which can be adjusted.
(2) Quinhydrone solution for Method 1.
(3) Combination calomel/platinum redox electrode.
(4) Thermometer.
(5) Flow-through cell, essential and not optional.

Procedure

(1) Measure DO with DO meter and if greater than 0.1 mg/L do not proceed with Eh measurement.
(2) Allow water to flow over quinhydrone solution bottle so that the groundwater to be measured and quinhydrone solution are at the SAME temperature.
(3) Check calomel electrode.
(4) Set up flow-through cell.
(5) Measure temperature of flowing groundwater which will be the same as the quinhydrone solution and record temperature.
(6) Look up in Table 5.4.1 the theoretical potential of quinhydrone solution relative to the hydrogen electrode at the recorded temperature record. (For example at 15 °C the theoretical potential is +300 mV).
(7) Immerse calomel electrode in the quinhydrone solution and using the *MILLIVOLT ADJUSTING KNOB* set millivolt reading at the theoretical potential. (In our example for 15 °C, at +300 mV).
(8) Rinse off electrode.
(9) Insert electrode through gland in flow-through cell, ensure there is no air in contact with the flowing groundwater.
(10) Take millivolt reading. This is the true electrode measured Eh of the groundwater.
(11) Rinse off electrode, thermometer and solution bottle and pack away.

Method 2

Identical to above method but with ZoBell solution exchanged for the quinhydrone solution. For our example at 15 °C the theoretical potential ZoBell solution is +450 mV, thus set meter at +450 mV and continue with procedure.

Theory update for method 3 and method 4

For methods 1 and 2 the millivolt adjustment knob was used to negate the relative potential of the calomel electrode which is +244 mV at 25 °C with respect to the standard hydrogen electrode which is designated to be 0 mV, i.e. using the millivolt adjustment knob make the calomel electrode mimic the standard hydrogen electrode and the calomel electrode relative potential is set at 0 mV. Table 5.4.3 shows the relative potential of the calomel/platinum electrode compared with the standard hydrogen electrode.

Table 5.4.3 **The relative potential of the calomel/platinum electrode compared with the standard hydrogen electrode at various temperatures**

t(°C)	E (mV)
0	260,2
5	257,4
10	254,1
15	251
20	247,7
25	244,4
30	241,1
40	234,3
50	227,2
60	219,9
70	212,4
80	204,7
90	196,7

Note that the potential of the electrode is determined by the temperature of the calomel half-cell mounted in the lower part of the electrode.

Thus, if there is no millivolt adjusting knob on the pH meter, the following procedure must be followed: measure the temperature of the solution, calculate the theoretical potential of the calomel electrode at that temperature in the solution being used, measure the potential in the solution and observe the difference, and then add the difference observed plus the calomel electrode potential to the observed reading of the groundwater to obtain the true electrode measured potential of the groundwater.

Method 3

Equipment

(1) pH meter which does NOT have a millivolt scale adjustment knob
(2) Quinhydrone solution
(3) Combination calomel/platinum redox electrode
(4) Thermometer
(5) Flow-through cell, essential and not optional

Procedure

(1) Measure DO with DO meter and if greater than 0.1 mg/L do not proceed with Eh measurement.
(2) Allow water to flow over the quinhydrone solution bottle so that the groundwater to be measured and the quinhydrone solution are at the SAME temperature.
(3) Check the calomel electrode.
(4) Set up the flow-through cell.
(5) Measure the temperature of the flowing groundwater which will be the same as the quinhydrone solution and record the temperature.
(6) Calculate the theoretical Eh of the calomel/platinum electrode to quinhydrone solution relative to the standard hydrogen electrode at that temperature. This is obtained by subtracting the mV values in Table 5.4.3 from those in Table 5.4.1 for that temperature. This is detailed below in Table 5.4.4 for a range of temperatures.

Table 5.4.4 Theoretical Eh of the calomel/platinum electrode to quinhydrone buffer pH 7 solution at various temperatures

Temperature (°C)	Calculation Table 5.4.1 minus Table 5.4.3	Theoretical Eh (mV)
25	+286 - (+244)	+42
20	+293 - (+248)	+45
15	+300 - (+251)	+49
10	+307 - (+254)	+53

(7) Measure the Eh of the quinhydrone buffer pH 7 solution which is at the same temperature as the flowing groundwater. Record the difference between the measured potential and the theoretical potential from step 6. If the difference is more than 10 mV the electrode is possibly faulty. Check the electrode by following the procedures outlined after Method 4. If this does not work, replace the electrode.
(8) Rinse off the electrode.
(9) Place the electrode in the flow-through cell, ensuring that there is no air in contact with the flowing groundwater.
(10) Take the millivolt reading and record.
(11) Calculate the true electrode measured potential of the groundwater which is the reading measured in step (10) plus the potential of the

calomel/platinum electrode for the observed temperature (this value is obtained from Table 5.4.3).
For example, the field procedure has recorded the groundwater temperature = 15 °C.
Groundwater potential (step 10) = -85 mV.
From Table 5.4.3 the electrode potential @ 15 °C = +251 mV.
Thus the true electrode measured potential of the groundwater is = (-85 mV) + (+251 Mv) = +166 mV.

(12) Rinse the electrode, quinhydrone solution bottle and thermometer and pack away.

Method 4

Identical to above method but ZoBell solution is used in place of quinhydrone buffer pH 7 solution. Step (7) is replaced by the following: Calculate the theoretical Eh of the Calomel/Platinum electrode to ZoBell solution relative to the standard hydrogen electrode at that temperature. This is obtained by subtracting the mV values in Table 5.4.3 from those in Table 5.4.2 for that temperature. This is detailed below for a range of temperatures.

Table 5.4.5 Theoretical Eh of the calomel/platinum to ZoBell solution

Temperature (°C)	Calculation Table 5.4.2 minus Table 5.4.3	Theoretical Eh (mV)
25	+428 - (+244)	+184
20	+439 - (+248)	+191
15	+450 - (+251)	+199
10	+461 - (+254)	+207

5.4.2.5 **TROUBLE-SHOOTING**

Platinum element

The platinum element must be kept clean and polished, especially for Methods 3 and 4 and preferably for Methods 1 and 2.

Platinum element contamination (After Kokholm)

Rinse the platinum element as follows:

(1) Rinse the surface of the platinum element with conc. H_2SO_4.

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

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

Calomel electrode contamination (After Kokholm)
These instructions are for the calomel electrode which uses saturated KCl solution as the salt bridge. If the calomel electrode does not use saturated KCl solution, then obtain the manufacturer's instructions and follow them.

- Air bubbles trapped in the KCl crystals
  Release the bubbles by tapping the electrode with a finger or by swinging it in circles by its lead, or heat the electrode in water bath to approximately 60 °C until sufficient KCl is dissolved to release the bubbles.

- KCl crystals in porous pin
  If KCl crystals in the porous pin are suspected, replace the KCl solution and, if necessary, immerse the electrode in water bath (60 °C) for 10 minutes.

- Protein contamination of porous pin
  Immerse the electrode in 5 % (v/v) hypochlorite solution for a few minutes and rinse with distilled water or soak the electrode in strong pepsin solution in 0,1 M HCl for some hours and rinse with distilled water.

- Oil or grease contamination
  Immerse the electrode in a solvent miscible with water (e.g., acetone) and clean with distilled water.

- Insoluble compounds (e.g. AgCl) deposited at the porous pin
  Polish the surface of the porous pin gently with emery paper.

- Sulphide contamination of the porous pin
  Seal the KCl filling hole and soak electrode for 24 hours in a solution of thiourea in 0,1 M HCl. Rinse with distilled water.

- Long-term exposure to concentrated solution
  Soak the electrode with tip in saturated KCl solution.

Storage of the electrode

Short-term storage

- Seal the KCl filling hole with a (moistened) rubber sealing ring or with paraffin film, e.g., *PARAFILM*.
- Immerse the electrode in saturated KCl solution.

Long-term storage

- Clean the electrode with distilled water and wipe it dry.
- Seal the KCl filling hole and the porous pin with a rubber sealing ring and rubber cap (moisten before mounting) or with paraffin film.

5.4.3 REFERENCES

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

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, pp. 925-927.

Lloyd, J.W. and J.A. Heathcote 1985 Natural inorganic hydrochemistry in relation to groundwater. Clarendon Press, Oxford.

Garrels, R.M. and C.L. Christ 1965 Solutions, minerals and equilibria. Freeman and Cooper C.O., San Francisco, 450 pp.

Hostettler, J.D. 1984 Electrode electrons, aqueous electrons, and redox potentials in natural water systems. American Journal of Science, 284, pp. 734-759.

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

Stumm, W. and J.J. Morgan 1981 Aquatic chemistry, 2nd. ed. Wiley-Interscience, New York, 780 pp.

Thorstenson, D.C. 1971 The concept of electron activity and its relation to redox potentials in aqueous geochemical systems. U.S. Geological Survey Open File Report 84-072, (microfiche), 24 pp.

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

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

5.5 DISSOLVED OXYGEN (DO)

5.5.1 INTRODUCTION

DO has a significant effect upon groundwater quality by regulating the valence state (and thus solubility) of, trace metals and by constraining the bacteriological metabolism of organic compounds in groundwater. For these reasons, the measurement of DO is important for groundwater quality investigations and especially so for groundwater pollution investigations.

"Oxygen's limited solubility is directly related to atmospheric pressure and inversely related to water temperature and salinity. The solubility of oxygen in water increases proportionately with hydrostatic pressure, i.e. depth. In dilute aqueous solutions at sea level, the solubility of oxygen ranges between 10.0 and 7.0 mg/L at temperatures ranging between 15 to 31 °C.

The most important chemical characteristic of molecular oxygen is its ability to oxidise or accept electrons from other species in water. 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 sulfide, ammonium, molecular nitrogen and other reductants. The most important aspect of these biochemical redox reactions is their irreversibility; therefore, dissolved oxygen is always consumed and never produced as a result of bacterial metabolism.

Dissolved oxygen concentration, in large part, controls the solubility of many naturally occurring, polyvalent trace elements in groundwater. For example, iron concentrations are usually below maximum drinking water standards in aerobic water due to the precipitation of iron oxyhydroxides. The oxyhydroxides, in turn, are important adsorbents of heavy metals.

Dissolved oxygen concentration should be considered a critical parameter in any investigation of groundwater contamination, particularly those involving the migration of landfill leachates or mining wastes. As previously mentioned, DO often controls the fate of dissolved organic contaminants by constraining the types and numbers of microorganisms 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 chlorobenzene groups are probably biodegradable in aerobic water while 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 sulfide. 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.

Nine of the 16 inorganic constituents that have specified concentration limits in drinking water (USA regulations) have multiple oxidation states and are therefore sensitive to DO concentration. These are arsenic, chromium, iron, mercury, manganese, selenium, uranium, nitrogen, and sulphur. Other potentially hazardous heavy metals such as silver, copper, cadmium and zinc form ionic complexes and solid compounds with multivalent elements, notably sulphur. Hence, the concentration of these heavy metals is also in part governed by DO concentration. Uranium, selenium, and arsenic are insoluble under reducing or anaerobic conditions. Conversely, iron and manganese are insoluble in aerobic water. 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". (Rose and Long, 1988)

5.5.1.1 DO AND Eh

If the groundwater sample has DO then the Eh can be calculated using the formula:

$$pE = 20{,}78 + \tfrac{1}{4}\log(P_{O_2}) - pH$$

where P_{O_2} is the partial pressure of O_2 and is calculated from the DO measurement and Henry's Law.

$$P_{O_2} = \frac{O_2 \text{ dissolved}}{K_{O_2}}$$

where K_{O_2} at 25 °C is $1{,}28 \times 10^{-3}$ mol/kPa.

At the detection limit of field DO meters, which is 0,01 mg/L, the calculated pE of water at pH 7 is 13,1, or expressed as Eh, is +780 mV. Water saturated with oxygen at pH 7 has a pE of 13,6. If the DO is close to or below detection limits then calculating Eh from DO is not possible and you must measure the Eh using an Eh probe and a pH meter which has millivolts reading capabilities.

5.5.2 METHOD OF DO MEASUREMENT

DO is measured using one of two methods:
(1) titration by modified Winkler titration; or
(2) with a DO electrode.

Under field conditions both methods give a precision of 0,1 mg/L and a detection limit of 0,2 mg/L. The DO electrode method is simpler but the equipment outlay is higher than for the titration method. Thus for a one-time investigation use the titration method, but otherwise invest in a DO meter and electrode which is much simpler and easier to use under field conditions.

5.5.2.1 MODIFIED WINKLER TITRATION

The iodometric test is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass-stoppered bottle. DO rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of thiosulphate (APHA, 1989).

Should you decide to use the titration method rather than the electrode method, first read APHA Standard Methods (APHA, 1989) and then consult with your analytical laboratory for equipment needs and methodology training. Do not be discouraged by this statement as the method is not complicated and is well-described in APHA, (1989).

If you are sampling at a pollution site where the dissolved ferrous iron concentration could be high, use the permanganate modification method as described in APHA, (1989). Also if measuring at a site with acid mine drainage where ferric iron concentrations will probably be high and cause interference, addition of potassium fluoride and azide will overcome the interference.

5.5.2.2 ELECTRODE METHOD FOR DO MEASUREMENT (Wood, 1981)

5.5.2.2.1 GENERAL PRINCIPLE

The sensing element of the DO meter is basically a polarographic system in which two solid metal electrodes in contact with an electrolyte are separated from the test solution by an oxygen-permeable membrane. The membrane serves as a diffusion barrier against impurities. The rate at which oxygen diffuses through the membrane is proportional to the pressure differential across the membrane. When oxygen diffuses through the membrane, it is rapidly consumed at the cathode. Thus, the rate of

diffusion is proportional to the absolute pressure of oxygen outside the membrane. When a suitable polarizing voltage 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 quantity of oxygen consumed. (Wood, 1981)

5.5.2.2.2 CALIBRATION OF INSTRUMENT

"For precise DO determinations, the meter should be calibrated before each use. Preferably, the calibration should be accomplished on the water under test. One sample of the water should be deoxygenated by adding an excess of sodium sulphite; a second sample should be aerated to saturation. The DO concentration of the air-saturated sample can be determined from Figures 5.5.1 and 5.5.2, provided the water temperature, barometric pressure, and altitude of the sampling site are known. If interfering substances are suspected in the natural sample, calibration should be accomplished on distilled water aerated to saturation. The interfering gas of importance in groundwater is H_2S.

In general, satisfactory calibration can be accomplished by using air-saturated water. In this procedure, the water sample is aerated by being shaken in the presence of air for 15-20 minutes.

Measure the water temperature. Figure 5.5.1 shows the DO concentration of air-saturated water at sea level as a function of temperature. Figure 5.5.2 shows correction factors that must be applied to the apparent oxygen concentration when the atmospheric pressure varies from 760 mm mercury. By use of these Figures, the correct value of oxygen dissolved in the air-saturated sample can be obtained and the meter calibrated". (Wood, 1981)

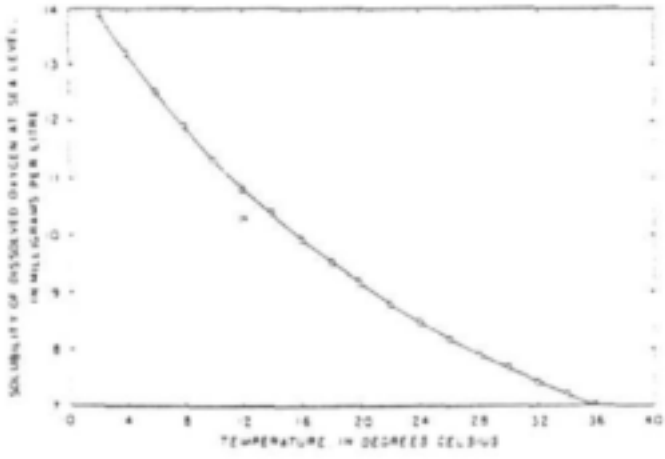

Figure 5.5.1 Solubility of oxygen in water at sea level as a function of temperature (Wood, 1981).

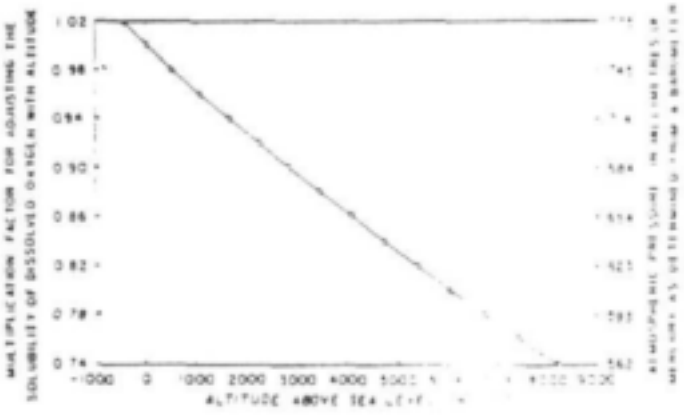

Figure 5.5.2 Correction [illegible] solubility of oxygen at differ[illegible] pheric pressures and altitud[illegible]

SUGGESTIONS

1. After calibration with aerated water, wave the electrode in the air. The wet electrode in contact with air will give the same reading as an air saturated sample of groundwater. If not, interfering substances are probably in the groundwater.

2. H_2S is common in polluted groundwater. In this situation DO values are essential to reconstruct and interpret actual ground- water chemistry. H_2S will affect the permeable membrane and tends to lower cell sensitivity. Eliminate this interference by frequently changing the membrane, replacing the electrolyte, and recalibrating the electrode.

5.5.3 EQUIPMENT CHECKLIST

(1) DO meter and electrode (with spare membranes, O-rings and electrolyte)
(2) Flow-through cell
(3) Thermometer
(4) Barometer
(5) Two 250 mL plastic bottles
(6) One 1000 mL plastic bottle for aeration of reference sample
(7) Saturated sodium sulphite solution
(8) Cobaltous chloride solution

5.5.4 FIELD PROCEDURE FOR ELECTRODE METHOD OF DO MEASUREMENT

(1) Pour a sample of the groundwater into a 250 mL plastic bottle to which has been added several mL of saturated sodium sulphite solution and a trace of cobaltous chloride. Replace cap and stir. This is the deaerated sample.
(2) Prepare the DO meter for calibration according to manufacturer's instructions.
(3) Switch the meter to the 0-10 position. Insert the electrode in the deaerated sample of Step 1. If the DO in the sample is greater than 0.0 mg/L, add saturated sodium sulphite in small increments until a reading of 0.0 mg/L is obtained. Add an excess of several mL after a reading of 0.0 mg/L is obtained.
(4) Pour a second sample of the groundwater into a 1 L plastic bottle and aerate for 5-10 minutes by shaking vigorously.
(5) Calculate the DO concentration of the aerated sample, by taking the barometric pressure and using Figures 5.5.1 and 5.5.2.
(6) Pour an aliquot of the aerated sample into a clean 250 mL plastic bottle. Switch the DO meter to the 0-10 position and insert the electrode in the aerated sample. To confirm this reading, wave the wetted electrode in the air. The two readings should be the same.
(7) With the calibration control, adjust the DO reading to the value obtained by step 5.

(8) Place the sensor in the flow-through cell. Gently open the flow control valve. Measure the *DO* concentration at about 5-10 minute intervals until a stable reading is obtained. Record the value to the nearest 0,1 mg/L. It is important not to have too high a flow-rate, otherwise a pressure-factor will be introduced which will give erroneous readings.
(9) Dismantle and wash the equipment with distilled water.

5.5.5 SAMPLING DEVICES SUITABLE FOR DO TESTING

Some methods of collecting the water sample for DO testing from the borehole are acceptable, whereas other methods are unacceptable or conditionally acceptable. These are summarized in Table 5.5.1, which is extracted from Rose and Long (1988). Note that the better methods are 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 5.5.1 Various sampling methods as they apply to monitoring dissolved oxygen

Sampling method or recovery mechanism	Acceptability of method	Comment
Natural spring	Conditionally acceptable	Sampling bottle should be held well below the spring orifice
Production well (pump in place)	Conditionally acceptable as a method of last resort	Intake level should be well below (metres) 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 (metres) the pumping water level; turbulence and pressure changes can result
Bailer	Generally unacceptable	Transfer of sample can disturb dissolved gases
Suction lift pump	Unacceptable	Outgassing is a strong possibility
Airlift	Unacceptable	Can oxygenate sample
Nitrogen displacement	Conditionally acceptable	May cause pressure changes
Gas-driven piston pump	Conditionally acceptable	May cause pressure changes
Bladder pump	Acceptable	Offers flexibility for choosing sampling depths

5.5.6 REFERENCES

APHA 1989 Standard methods for the examination of water and wastewater, 17th Edition Washington, D.C., Am. Public Health Assoc.

Rose, S. and A. Long 1988 Monitoring dissolved oxygen in groundwater: Some basic considerations. Ground Water Monitoring Review, Winter 1988.

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.

5.6 ALKALINITY

If the investigation you are involved in requires an understanding of the chemical equilibrium related to carbonate minerals it is essential to obtain accurate values of pH, carbonate concentration and bicarbonate concentration of the groundwater. In such cases, either conduct a carbonate and bicarbonate (titration) determination in the field or analyse the sample in the laboratory within two hours of collection, having measured the pH at the time of collection. (The latter procedure is recommended and of course it makes the task of the field sampler easier).

Investigations requiring this procedure 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
- calcite ($CaCO_3$) encrustation reduction.

The equipment needed is:

(1) all the reagents and meters for pH measurement
(2) 25 mL burette
(3) 25 and 50 mL pipette
(4) portable magnetic electric stirrer
(5) stands, clamps, beakers
(6) 0,01*N* hydrochloric acid
(7) a well-padded box to prevent breakage.

As can be seen from the above list this equipment is not easily obtained off-the-shelf. Thus if you intend to conduct such an investigation and need to titrate in the field, do the following.

STEP 1 Read up the theory and practice.

A: Theory:

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

This is excellent description of the subject and is easy to read.

B: Theory:

Lloyd, J.W. and J.A. Heathcote 1985 Natural inorganic hydrochemistry in relation to groundwater. Clarendon Press, Oxford.

C: Theory and practice:

Wood, W.W. 1976 Guidelines for collection and field analysis of groundwater samples for selected unstable constituents. Chapter D2, Techniques of Water-Resources Investigation, Chapter D2, US Geological Survey.

D: Theory and practice:

Barnes, I. 1964 Field measurements of alkalinity and pH: U.S. Geological Survey Water-supply Paper 1535-H, 17p.

STEP 2

Acquire the equipment from the analytical laboratory. Following the above descriptions which are comprehensive and complete, carry out field titrations.

Conducting field alkalinity titrations is not difficult - do not be put-off by the apparent complexity. If you are doing alkalinity titrations for the first time, carry out a few titrations in the laboratory under supervision before doing them in the field.

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, namely, 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).

- **Blanks**. 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. This 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.

- If using the same sampling pump for several pollution monitoring boreholes, collect a **field blank**. Choose one of the boreholes showing the highest level of contamination, decontaminate the sampling equipment (Chapter 17), and then collect a sample of the final rinse water, which is the field blank.

- Prepare **spiked samples** and send them to the laboratory. These are usually prepared by the analytical laboratory who adds a known quantity of the chemical or contaminant to a typical but "clean" groundwater sample. The field scientist takes the spiked sample into the field, puts it into a standard sample bottle marked as if it were a borehole sample and returns it with the rest of the water samples to the laboratory.

- Ensure that **quality control standards** are used by the analytical laboratory. A quality control standard is a typical groundwater 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 the laboratory being used does not have/use a QC standard either change laboratory or prepare your own standard. On the pilot sampling run, collect in a 20 L container 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.

  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 Standard Methods (1989) and also 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 interlaboratory comparison samples.

In South Africa, the CSIR conducts a nation-wide interlaboratory comparison study. This programme is open to participation by all laboratories who analyse water and wastewater samples. Use only a laboratory that regularly participates.

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 (1989) and Canter *et al.* (1987).

6.4 REFERENCES

APHA 1989 Standard methods for the examination of water and wastewater; 17th Edition Washington, D.C., Am. Public Health Assoc.

Canter, L.W., R.C. Knox and D.M. Fairchild 1987 Ground water quality protection. Lewis Publishers, 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

This is a very important part of any sampling programme, as the guide defines specific aims of the programme, which can vary tremendously from project to project. Things to be considered by monitoring programme designers are cost, time, effective sampling, significant parameters, laboratory requirements 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.

The Monitoring Programme Guide must include the following:

- 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.
- Owner of the site.
- 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.
- 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 - 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.

CHAPTER 8

SAMPLE RECORDS AND CHAIN OF CUSTODY

Inadequate information regarding the circumstances during sample collection and subsequent handling of the sample, i.e. chain of custody, may render any resulting data useless. Especially in sampling programmes 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. The sections 8.1 and 8.2 are extracted from Scalf *et al.* (1981) who in turn abstracted the information from the U.S. EPA (1977).

8.1 SAMPLE RECORDS

- Sample description - type (groundwater, surface water), volume;
- Sample source - well number, location;
- sampler's identity - chain of evidence should be maintained; each time transfer of a sample occurs, a record including the signatures of parties involved in the transfer should be made. (This procedure can have legal significance);
- time and date of sampling;
- significant weather conditions;
- sample laboratory number;
- pertinent well data - depth, depth to water surface, pumping schedule, and method;
- sampling method - vacuum, bailer, pressure;
- preservatives, (if any) - type and number (e.g. NaOH for cyanide, H_2SO_4 for phenols, etc.);
- sample container - type, size, and number (e.g. 3 L glass stoppered bottles, 1-gallon screw-cap, etc.);
- reason for sampling - initial sampling of new landfill, annual sampling, quarterly sampling, special problem sampling in conjunction with contaminant discovered in nearby domestic well, etc.;

- appearance of sample - colour, turbidity, sediment, oil on surface, etc.;

- any other information which appears to be significant - (e.g. sampled in conjunction with state, county, local regulatory authorities; samples for specific conductance value only; sampled for key indicator analysis; sampled for extended analysis; re-sampled following engineering corrective action, etc.);

- name and location of laboratory performing analysis;

- sample temperature upon sampling;

- thermal preservation - (e.g. transportation in ice chest);

- analytical determinations (if any) performed in the field at the time of sampling and results obtained (e.g. pH, temperature, dissolved oxygen and specific conductance, etc.);

- analyst's identity and affiliation.

8.2 CHAIN OF CUSTODY

- As few people as possible should handle the sample.

- Samples should be obtained by using standard field sampling techniques, if available.

- The chain of custody records should be attached to the sample container at the time the sample is collected, and should contain the following information: sample number, date and time taken, source of the sample (includes type of sample and name of firm), the preservative and analysis required, name of person taking sample, and the name of witness. The prefilled side of the card should be signed, timed, and dated by the person sampling. The sample container should then be sealed, containing the regulatory agency's designation, date, and sampler's signature. The seal should cover the string or wire tie of the chain of custody record, so that the record or tag cannot be removed and the container cannot be opened without breaking the seal. The tags and seals should be filled out in legible handwriting. When transferring the possession of samples, the transferee should sign and record the date and time on the chain of custody record. Custody transfers, if made to a sample custodian in the field, should be recorded for each individual sample. To prevent undue proliferation of custody records, the number of custodians in the chain of possession should be as few as possible. If samples are delivered to the laboratory when appropriate personnel are not there to receive them, the samples should be locked in a designated area within the laboratory so that no one can tamper with them.

- Blank samples should be collected in containers, with and without preservative, so that the laboratory analysis can be performed to show that there was no container contamination.

- A field book or log should be used to record field measurements and other pertinent information necessary to refresh the sampler's memory in the event that he later becomes a witness in an enforcement proceeding. A separate set of field notebooks should be maintained for each survey and stored in a place where they can be protected and accounted for at all times. A standard format should be established to minimize field entries and should include the types of information listed above. The entries should then be signed by the field sampler. The responsibility for preparing and retaining field notebooks during and after the survey should be assigned to a survey coordinator or his designated representative.

- The field sampler is responsible for the care and custody of the samples collected until properly dispatched to the receiving laboratory or turned over to an assigned custodian. He must assure that each container is in his physical possession or in his view at all times or stored in a locked place where no one can tamper with it.

- Photographs can be taken to set forth exactly where the particular samples were obtained. Written documentation on the back of the photograph should include the signature of the photographer, the time, date, and site location. Photographs of this nature, which may be used as evidence, should be handled according to the established chain of custody procedures.

- Each laboratory should have a sample custodian to maintain a permanent log book in which he records for each sample the person delivering the sample, the person receiving the sample, date and time received, source of sample, sample number, how transmitted to the laboratory, and a number assigned to each sample by the laboratory. A standardized format should be established for log-book entries. The custodian should ensure that heat-sensitive or light-sensitive samples or other sample materials having unusual physical characteristics or requiring special handling are properly stored and maintained. Distribution of samples to laboratory personnel who are to perform analyses should be made only by the custodian. The custodian should enter into the log the laboratory sample number, time, date, and the signature of the person to whom the samples were given. Laboratory personnel should examine the seal on the container prior to opening and should be prepared to testify that their examination of the container indicated that it had not been tampered with or opened.

8.3 FIELD SAMPLING RECORD FORMS AND CHAIN OF CUSTODY FORMS

An example of these forms are included in the plastic pocket at the end of this manual. The example is used by Wisconsin State, U.S.A. (Wisconsin, 1987). Either copy and use these forms or design and use your own.

8.4 REFERENCES

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby and J.Fryberger 1981 Manual of ground-water sampling procedures. National Water Well Association, Worthington, Ohio.

U.S. EPA 1977 Procedures manual for ground water monitoring at solid waste disposal facilities. U.S. Environmental Protection Agency, EPA/530/SW-611, 269 p.

Wisconsin Department of Natural Resources 1987 Groundwater sampling procedure field manual. Publ. WR-168-87. P.O.Box 7921, Madison, WI 53707.

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

Major sources of error will 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. For specialised analyses such as heavy metals and organic compounds the sample bottle preparation is more involved. Each section of Chapter 4, Determinand Selection, has a paragraph on sample bottle preparation which must be strictly and routinely adhered to in order to produce meaningful results. Chapter 2 has a summary table which details what containers and caps can be used.

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 with and after writing cover with a clear adhesive tape. (3M 72 mm wide Transparent Tape works well).

Included on the bottle label should be the following:

Sample ID no
Sample site
Date of sampling
Field pH, Eh, DO, temperature and alkalinity
Sample identity.

9.4 SAMPLE SIZE

The golden rule is to confirm with the analytical laboratory before going into the field, what volume of water sample they need. 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 return to the field. 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 laboratory I use requests 3 x 250 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 3 months after the analytical results have been posted in case of any queries concerning the analysis.

9.5 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.

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, change 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.

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

Preservative	Action	Applicable to:
$HgCl_2$	Bacterial inhibitor	Nitrogen forms, phosphorus forms
Acid (HNO_3)	Dissolves metals, prevents precipitation	Metals
Acid (H_2SO_4)	Bacterial inhibitor	Organic samples (COD, oil and grease, organic carbon)
	Salt formation with organic bases	Ammonia, amines
Alkali (NaOH)	Salt formation with volatile compounds	Cyanides, organic acids
Refrigeration	Bacterial inhibitor	Acidity - alkalinity, organic materials, BOD, colour, odour, organic P, organic N, carbon, etc., biological organism (coliform, etc.)

9.6 FURTHER READING

American Society for Testing Materials 1969 Manual on water, ASTM Special Technical Publication, No. 442.

Everett, G.L. 1980 Groundwater monitoring. Genium Publishing Corporation, Schenectady.

Wisconsin Department of Natural Resources, September 1987 Groundwater sampling procedure field manual. Publ. WR-168-87. P. O. Box 7921, Madison, WI53707.

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, Ontario. Prepared for: Environmental Affairs Department American Petroleum Institute.

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.

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

1. If the water-level measuring device cannot go down the borehole, the pump will also not be able to go down.

2. 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.

3. The volume of water that must be purged must be calculated so that a representative sample can be collected.

4. Water-levels are essential for calculating groundwater flow directions and seasonal changes of the aquifer.

10.2 WATER-LEVEL MEASURING EQUIPMENT

The apparatus of choice is a twin-core cable mounted on a hand-winch. The end of each wire is bared so that the open contacts are ~50 mm apart. A weight is hung below the bared ends. At the top end the circuit is completed with either :

1. an ohm meter (using a multimeter)
2. or a fitted milliamp meter (0-1,0 mA)
3. or a buzzer
4. 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.

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 and errors can be made when adding the whole metres to the fractions of the final metre.

3. Mark the cable, remove from the borehole and measure with a tape. This is not preferred as it requires two persons.

10.3 FIELD PROCEDURE

1. Lower the end down the borehole until the needle deflects, the buzzer or light goes on, and 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. Remove the cable and clean off any rust or oil.

6. If each borehole is properly purged and sampled in order i.e. from least to most contaminated, there is no need to decontaminate your water-level cable until the final borehole. If not, then clean it thoroughly before doing anything else.

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. This review paper is comprehensive and complete. I have added some minor additional notes and comments at the end of the reprint.

Generalized Ground Water Sampling Device Matrix[1]

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 parameters (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[R], polyethylene, glass.

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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[R]

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[R], polycarbonate, Delrin[R].

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[R], silicone, Viton, Neoprene[R], 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, aluminum 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 practical 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 rocks or multilevel aquifers may call for in-situ sampling devices as mentioned in notes. Suitabilities based on currently available information and subject to change.

						GROUND WATER PARAMETERS														
						INORGANIC							ORGANIC				RADIOACTIVE		BIOL.
		Device	Approximate Maximum Sample Depth	Minimum Well Diameter	Sample Delivery Rate or Volume	EC	pH	Radon	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	200 ft	50 mm	0 - 2 L/min									*					
		Bladder pump	400 ft	38 mm	0 - 7.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	*
		Helical rotor	160 ft	50 mm	0 - 4.5 L/min	*	*	*	*	*	*	*	*	*	*	*	*	*	
		Piston pump (gas-drive)	300 ft	38 mm	0 - 2 L/min	*			*	*	*		*				*	*	
		Centrifugal	Variable	75 mm	variable	*			*		*						*	*	
	SUCTION LIFT	Peristaltic	26 ft	12 mm	0.04 - 1.1 L/min	*			*		*		*				*		*
	GAS CONTRACT	Gas-lift	variable	25 mm	variable														
		Gas-drive	150 ft	25 mm	0.75 L/min	*			*		*		*				*		
IN SITU SAMPLING (4 Vols 3.5		Pneumatic	no limit	not applicable	0.04 - 0.5 L	*	*	*	*	*	*		*				*	*	*

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

Sample 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 rate should be carefully controlled to prevent excessive degassing of the sample.

* Indicates device is portable, suitable for application (pumping device purchased not specified properly and is constructed of suitable materials).

REFERENCES

Barcelona, M.J., J.A. Helfrich, E.E. Garske and J.P Gibb 1984 A laboratory evaluation of groundwater sampling mechanisms. *Ground Water Monitoring Review*, 4, (2), pp.32-41.

Blegen, R.P., K.F. Pohlmann and J.W. Hess 1987 Bibliography of groundwater sampling methods. U.S. environmental Protection Agency Internal Report EPA 600/X-87/325, 43 pp.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry 1983 Groundwater monitoring and sample bias. American Petroleum Institute, Environmental Affairs Department, 206 pp.

Houghton, R.L. and M.E. Berger 1984 Effects of wellcasing composition and sampling method on apparent quality of ground water. In: *Proceedings of the Fourth National Symposium and Exposium on Aquifer Restoration and Ground Water Monitoring*, Columbus, Ohio, National Water Well Association, Water Well Journal Publishing Co., Dublin, Ohio, pp.203-213.

Imbrigiotta, T.E., J. Gibs, T.V. Fusillo, G.R. Kish and J.J. Hochreiter 1986 Field evaluation of seven sampling devices for purgeable organic compounds in ground water. Prepared for ASTM Symposium on Field Methods for Ground Water Contamination Studies and Their Standardization, February 2-7, 1986, Cocoa Beach, Florida, 23 pp.

Muska, C.F., W.P. Colven, V.D. Jones, J.T. Scogin, B.B. Looney and V. Price Jr. 1986 Field evaluation of ground water sampling devices for volatile organic compounds. In: *Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring*, Columbus, Ohio, National Water Well Association, Water Well Journal Publishing Co., Dublin, Ohio, pp 235-246.

Nielsen, D.M. and G.L. Yeates 1985 A comparison of sampling mechanisms available for small-diameter ground water monitoring wells. *Ground Water Monitoring Review*, 5, (2), pp.83-98.

Pearsall, K.A. and D.A.V. Eckhardt 1987 Effects of selected sampling equipment and procedures on the concentrations of trichlorethylene and related compounds in ground water samples. *Ground Water Monitoring Review*, 7, (2), pp. 64-73.

U.S. Environmental Protection Agency 1986 RCRA ground-water monitoring technical enforcement guidance document, Office of Water Programs Enforcement, Office of Solid Waste and Emergency Response OSWER-9950.1, 208 pp. + appendices.

U.S. Environmental Protection Agency 1987 Handbook: *Groundwater*. EPA/625/6-87/016, 212 pp.

NOTE: For this manual the units of the original article have been converted to S.I. units.

11.2 SOME ADDITIONAL COMMENTS AND NOTES

Bladder pump - As can be seen from the matrix table the bladder pump, especially when constructed entirely from Teflon, is suitable for sampling for all parameters. The bladder pump has the advantage over the helical rotor which is the only other all-rounder (almost, excepting 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 R1 500 (1990 cost imported from U.S.A.). The complete set-up which includes a surface pulse controller, the pump and all air-lines costs R5 500. The cost of the air supply is not included. This could be a bought or hired compressor, a set of SCUBA bottles or nitrogen gas bottles. The bladder pump is the method of choice.

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. 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.

Syringe samplers - The same comments for the point-source bailer apply.

11.3 FURTHER READING

Canter, L.W., R.C. Knox and D.M. Fairchild 1987 Ground water quality protection. Lewis Publishers, Michigan.

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.

Pohlman, K.F. and J.W. Hess 1988 Generalized ground water sampling device matrix. Ground Water Monitoring Review, NWWA, Ohio.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby and J. Fryberger 1981 Manual of ground-water sampling procedures. National Water Well Association, Worthington, Ohio.

CHAPTER 12

PURGING THE BOREHOLE

12.1 INTRODUCTION

A borehole must first be purged to remove stagnant water from the borehole so that the groundwater sample subsequently collected is representative of the *in situ* groundwater. Stagnation modifies groundwater chemistry to the extent that samples may be totally unrepresentative of the formation water. Stagnant water will be affected by a number of processes:

- Leaching or adsorption of certain constituents from or onto the borehole casing or screen.
- 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).
- Precipitation or dissolution of certain metals due to changes in the concentration of certain dissolved gases such as oxygen and carbon dioxide.
- Addition of foreign materials through the top of the borehole.
- Loss of VOCs.
- Changes of redox potential due to contact 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.

Purging of the borehole in practice involves the removal of sufficient water so that the field chemistry parameters (pH, EC and Eh) are stable. For most cases, this involves the removal of three times the volume of the standing water in the borehole. As soon as pH and EC are stable for the duration of the purging of one borehole volume, start sampling.

12.2 FIELD PROCEDURE

1. Measure the water-level
2. Measure the borehole depth
3. Thus height of water column = borehole depth - depth to water-level.
4. Calculate the standing volume of water in litres by substituting in the following formula.

$$\text{Volume of standing water} = \pi \times (\text{radius of borehole in metres})^2 \times \text{Height of water column in metres} \times 1000$$

5. Install pump with inlet close to static water level for a high-yielding borehole. (For a low-yielding borehole see Chapter 13)

6. Set up EC, pH and Eh 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 EC, pH and Eh

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 EC, pH and Eh have not stabilized (this is uncommon), continue pumping until it stabilizes. 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

14. Once the borehole has been purged, with the pump still pumping, lower the pump a short distance, 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. See Figure 12.1

15. Collect the required groundwater samples

16. If the site is a hazardous waste site make arrangements to safely dispose of the purged water which may or may not contain toxic substances. Collect the purged water in the pre-organised containers and dispose safely.

12.3 LOW-YIELDING BOREHOLES

Some boreholes to be sampled are low-yielding and go dry when purging. 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. Bladder pumps are very useful in such cases as the pumping rate can be adjusted to pump as low as 1 L/minute. Low-yielding boreholes pumped at high rates will give erroneous results for parameters affected by exposure to air, especially Eh.

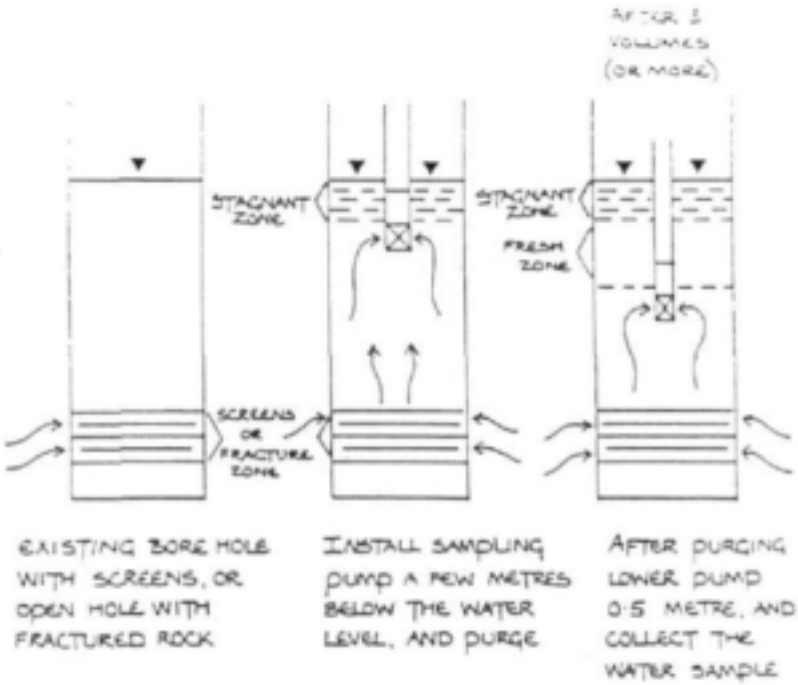

FIGURE 12·1
SKETCH SHOWING METHOD OF POSITIONING THE SAMPLING PUMP IN A BORE HOLE, IN ORDER TO AVOID CONTAMINATING THE WATER SAMPLE WITH STAGNANT WATER (AFTER ROBIN AND GILLHAM, 1987).

12.4 TURBID WATER

If the borehole water becomes turbid or is silty, the borehole should be re-developed before the next sampling run. This can be caused by purging too rapidly, so reduce rate to see whether turbidity reduces.

12.5 PURGING EQUIPMENT

Submersible pumps, bladder pumps and air-lift pumps are suitable. Bailers, grab samplers and syringe devices are not suitable.

NOTE: If purging by air-lifting, the measurement of pH will be futile. In this case monitor EC and purge at least three well-volumes. After purging by air-lifting, the water sample can be collected by bailer or syringe.

12.6 TO PURGE OR NOT TO PURGE: THE DEBATE

There are two reasons why a groundwater quality investigator promotes the idea that a borehole should not be purged:

1) He/she does not possess the equipment to sample groundwater properly (The standard and only sampling equipment of these operators is a bailer);
2) He/She is unwilling to purge and sample the well properly.

The one and only time that a sample should be collected before purging takes place is to observe whether or not floating and/or sinking organic compounds such as dieseline, 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 can be measured. For sinking chlorinated solvents 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 an indication of the degree of contamination, but only give a yes/no answer.

12.7 REFERENCES

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.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry 1985 Field evaluation of well flushing procedures. Department of Earth Sciences, University of Waterloo, Ontario. Prepared for Environmental Affairs Department, American Petroleum Institute.

Robin, M.J.L. and R.W. Gillham 1987 Field evaluation of well purging procedures. Ground Water Monitoring Review, NWWA Ohio.

Panko, A.W. and P. Barth 1988 Chemical stability prior to ground-water sampling: A review of current well purging methods. Ground-Water Contamination: Field Methods, ASTM STP 963, A.G. Collins and A.I. Johnson, Eds., American Society for Testing and Materials, Philadelphia.

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.

CHAPTER 13

FILTERING DEVICES

13.1 INTRODUCTION

Groundwater samples for iron, manganese, heavy metals, phosphate and onsite alkalinity determinations must be filtered onsite. The general procedure is to collect the unfiltered samples and then the filtered sample.

13.2 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, thus vacuum filtering is not recommended and will not be discussed any further. Pressure filter devices are either in-line or syringe type.

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 is recommended for iron, manganese and heavy metals.

The alternate device is a hand-held syringe system. This device has a two-way valve and a double piston cylinder. 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 will cause no discernible bias.

13.3 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 slower clogging and thus faster filtering.

Filters come in a variety of pore sizes, ranging from 0,1 to 2.0 micron. The standard pore size that MUST be used for groundwater sample filtration is 0,45 micron. This filter will remove all silt, most clay, most bacteria and a large portion of the iron and manganese oxyhydroxides. Viruses and large organic molecules such as humic and fulvic acids will not be removed. If the water is particularly muddy, use a pre-filter i.e. a 1 or 2 micron filter placed on top of the 0,45 micron filter.

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 (Geotech).

A useful alternate filter device is the disposable in-line filter. It is available in 0,45 micron pore size and either standard size for normal groundwater or as high-capacity for large volumes or highly turbid samples.

13.4 GENERAL FIELD PROCEDURE

1. Rinse the filter device with deionized water.
2. Insert the filter membrane correct side up, usually the side with the printed grid.
3. Connect in-line or draw up a sample into the syringe filter.
4 Discard the first 50 L.
5. Collect the required amount of filtered sample.
6. Discard filter membrane in wastebag - do not litter.
7. Disassemble filter apparatus and rinse clean with deionised water.

13.5 REFERENCES

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

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.

QED brochures. QED Groundwater Specialists, P.O Box 3726 Ann Arbor, M148106.

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

CHAPTER 14

FLOW-THROUGH CELL

In order to measure the field parameters pH, Eh and EC without exposing the groundwater to the atmosphere, it is necessary to use a flow-through cell. A flow-through cell is a closed box with groundwater flowing in at the bottom and out of the top so that no air is trapped. The pH, Eh and EC probes are inserted into the flowing water through water-proof glands in order to take the field readings. The design of flow-through cells is many and varied. A recommended design is that of Garske and Schock (1986). The advantages of this design are:

- clear sides so that the coating of electrodes with bubbles, colloidal material or mineral precipitates can be monitored;
- the conical shape minimizes the trapping of air bubbles that is common with others cells;
- the relatively large diameter if combined with a slow rate of through-flow reduces "stream potential", which will lead to erroneous pH readings.

The combination of this cell with a valving system will aid in-line filtration and sampling after the field measured parameters have stabilized.

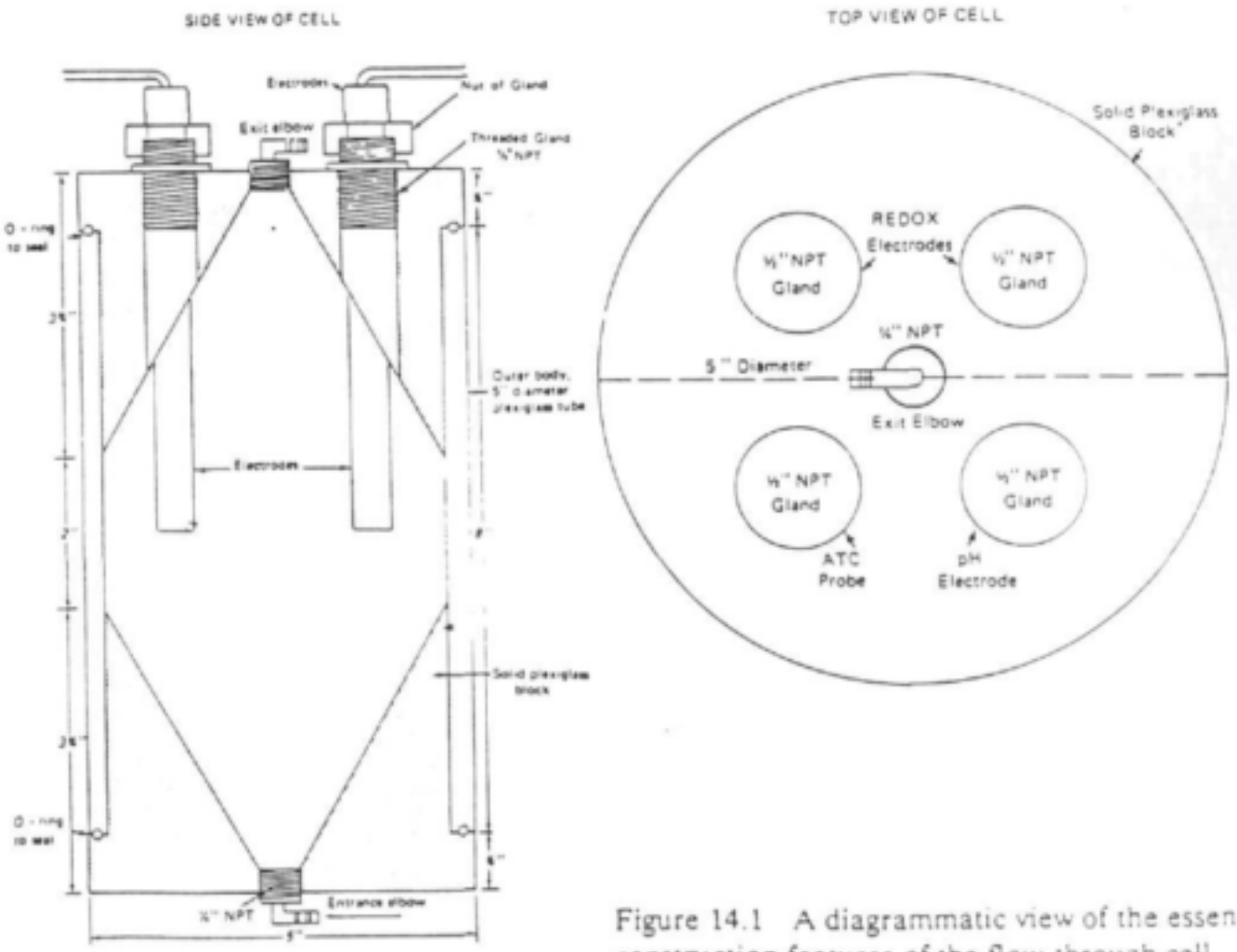

Figure 14.1 A diagrammatic view of the essential construction features of the flow-through cell.

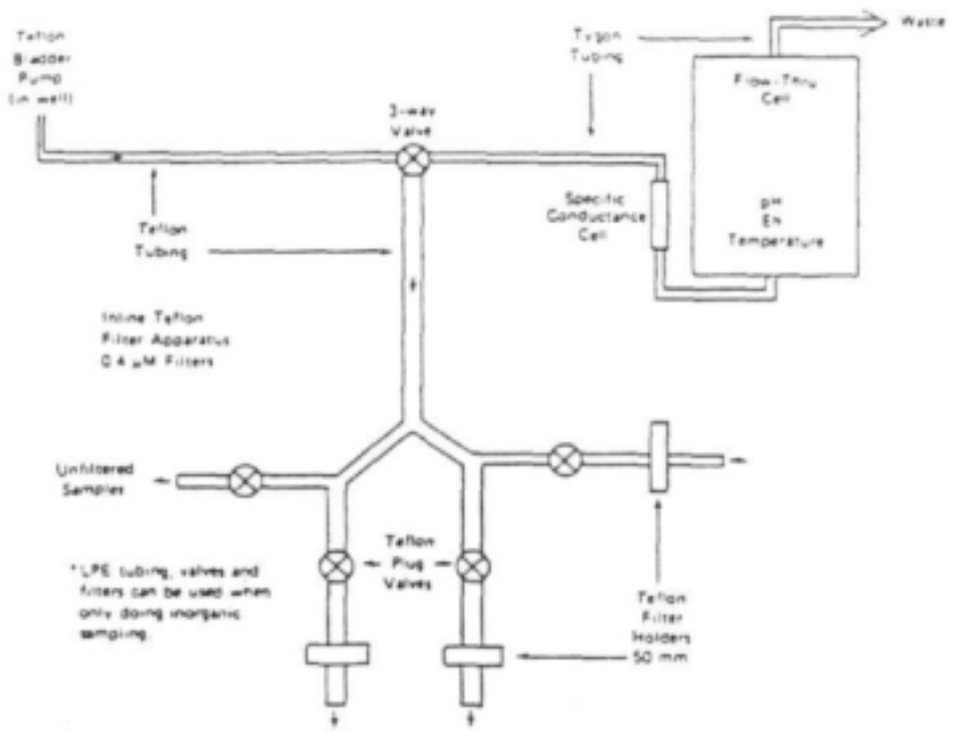

Figure 14.2 Diagram of valving and sampling system enabling in-line filtration of water samples, and sequential switching of membrane filters if they clog.

14.1 REFERENCE

Garske E.E. and M.R. Schock 1986 An inexpensive flow-through cell and measurement system for monitoring selected chemical parameters in groundwater. Groundwater Monitoring Review, 2, 1986, NWWA, Ohio.

CHAPTER 15

MULTIPLE LEVEL SAMPLING

15.1 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 15.1 shows the effect of simple, layered heterogeneities on chemical transport patterns.

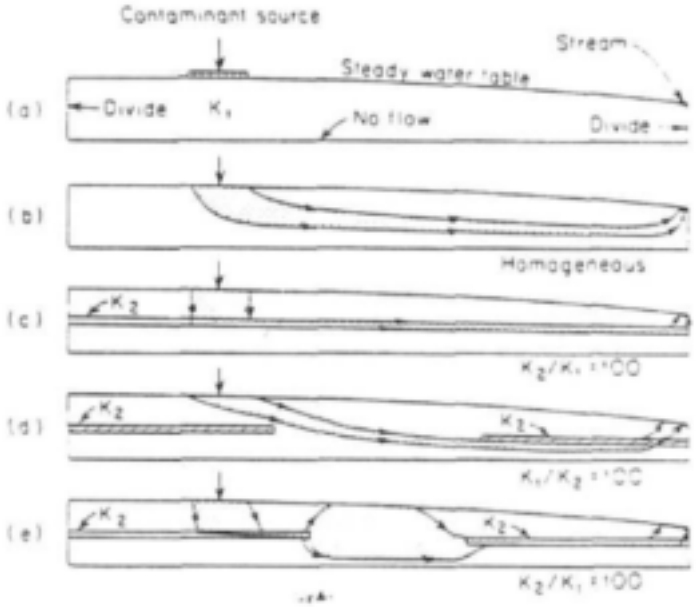

Figure 15.1 **Effect of layers and lenses on flow paths in shallow steady-state groundwater flow systems. (a) Boundary conditions; (b) homogeneous case; (c) single higher-conductivity layer; (d) two lower-conductivity lenses; (e) two higher-conductivity lenses (Freeze and Cherry, 1979, 397)**

15.2 METHODS OF CONSTRUCTION OF MULTILEVEL SAMPLING INSTALLATION

Multilevel sampling installations are grouped into three methods of construction and are illustrated in Fig 15.2.

1. Multiple monitoring wells at one site.
2. Single monitoring well with multiple screens and piezometers.
3. Single monitoring well with a single long screen "Flow-through" well.

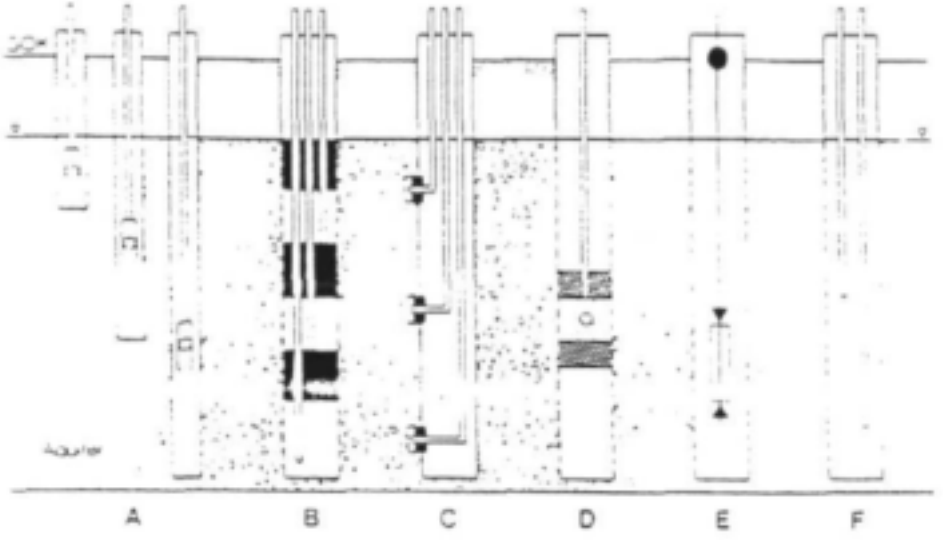

Figure 15.2 Types of monitoring wells and sampling devices (After UNESCO, 1972)

Version A - This is a group of monitoring wells at the same site. Each well 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.

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 bentonite 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 (not suitable for gases and VOCs). If greater than 8 metres then the piezometers will have to be 50 mm to 65 mm OD in order to accept a down-the-hole 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 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.

Versions D, E and F - The borehole is completed with one long screen for unconsolidated material or is open-hole construction for hard-rock. For Version D - An inflatable packer is moved to various positions and a sample is pumped from between the packers. For Version E - The depth-specific 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.

Versions D, E and F are termed "Flow-through" wells by Gillham *et al.* (1983) who seriously question the validity of the hydrochemical results obtained and state - "In general, the flow-through assumption is difficult to verify and raises several questions concerning the suitability of these types of installations. The main argument which seems to support the concept of the flow-through well is that constant composition profiles have been observed in these wells from one sampling session to another. It would seem, however, that this observation would be more indicative of a state of equilibrium where the water is sampled in a consistent manner, rather than providing assurance of an undisturbed composition profile. In view of the fact that the hydraulic conductivity inside the well is infinitely larger than the hydraulic conductivity of any formation, the flow-through assumption seems hard to support. Any slight vertical component to the hydraulic gradient in the aquifer around the well would contribute to some degree of vertical movement (and thus mixing) inside the well. In practice, this type of situation is the rule rather than the exception and there are therefore very few instances in which this type of sampling well can be used with a high degree of confidence. In addition, if vertical flow does occur in the well, the well could spread contaminants to regions that were previously uncontaminated."

A subsequent investigation by Rödelsperger *et al.* (1991) produced proof of this view. In this investigation of an unconsolidated aquifer nitrate at 150 mg/L was found in a series of three shallow wells and a suction cup. However, in a shallow (6 m) well adjacent to a deep (30 m) well 30 mg/L of nitrate was observed rather than the 150 mg/L which was expected. The following is extracted verbatim from this report.

15.3 SAMPLING WITH AND WITHOUT STATIONARY PACKERS

(RÖDELSPERGER *et al.*, 1991)

"The importance of this equipment is demonstrated by the results described below. Figure 15·3 shows a constellation of one deep and several shallow observation wells, an irrigation well, and a suction cup reaching to the saturated zone. The nitrate concentrations of the near-surface groundwater in this area are plotted below (solid bars).

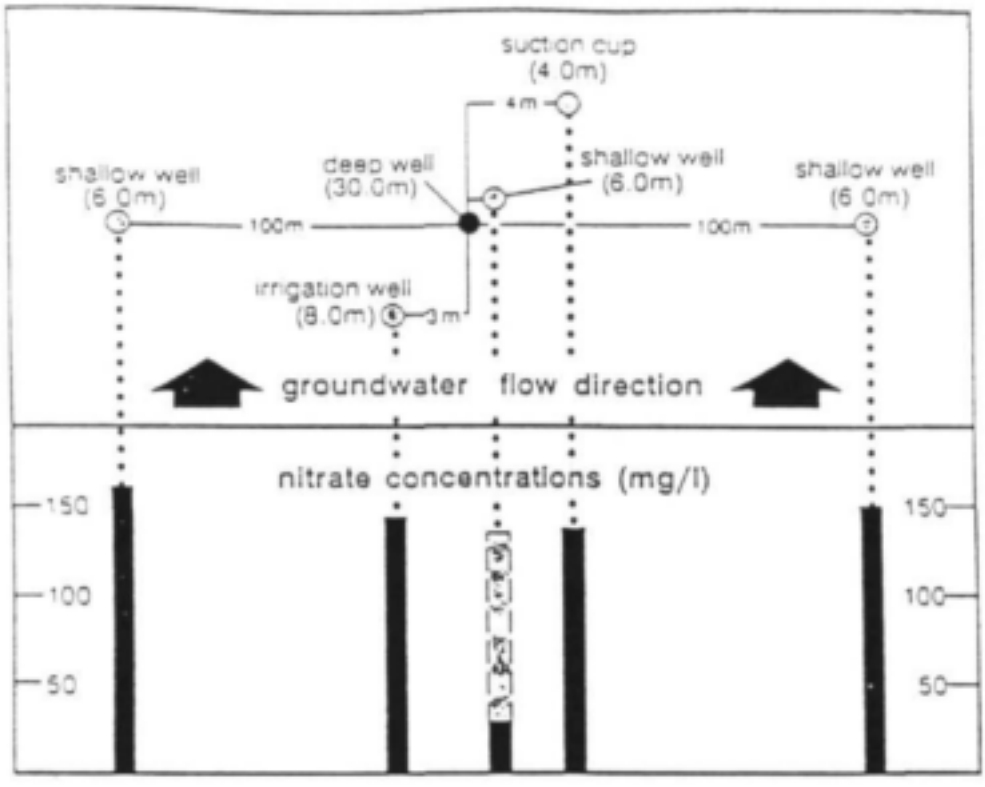

Figure 15.3 Influence of vertical groundwater displacement inside a deep observation well on the concentrations near the groundwater surface in its vicinity (Rödelsperger et al., 1989)

With the exception of the shallow well in immediate vicinity to the deep observation well, nitrate concentrations of about 150 mg/L were found in all shallow sampling devices. At first sight, a narrow stream of low-concentrated groundwater seemed to flow, which was seized by the shallow well but not by the irrigation well or the suction cup. This curious phenomenon was caused by inhomogeneous hydraulic permeabilities of the aquifer. Low-concentrated groundwater from deeper layers of the aquifer was displaced upwards through the pipe of the deep observation well that acted as a short circuit with respect to the various pressure heads in different depths. Indeed, three weeks after the deep observation well was equipped with a multipacker system as described above, the shallow well in its proximity showed the same nitrate concentrations as should be expected from the other results (dotted bar).

The deep observation well mentioned before may also quote as an example for the difficulties to carry out a representative sampling in deep aquifers with inhomogeneous structure using a doublepacker system. In figure 15.4, the nitrate profiles obtained with a doublepacker (dotter line) are contrasted with the results from layerwise sampling with the stationary multipacker system (solid line). The difference is obvious: Before the well was equipped with stationary packers, a large volume of upflowing, low concentrated water could infiltrate into the upper

parts of the aquifer, and even after a long pumping period the original groundwater could not be seized by the doublepacker system. Using the stationary multipacker system, the originally existing, distinct nitrate profile was detected. The presented result is not an individual case, but could be observed in a similar form at wells in the same and in other observation areas".

Figure 15.4 Vertical nitrate profiles in the aquifer by layerwise sampling - comparison between sampling with a doublepacker system (dotted line) and sampling after the equipment of the well with stationary packers (solid line) (Rödelsperger et al., 1989)

15.4 SQUTH AFRICAN CONSIDERATIONS

In South Africa most boreholes are completed in secondary aquifers or hard-rock and are thus open-hole construction. Those boreholes with two or more water-strikes are likely to be "flow-through" wells. Thus the results of all groundwater quality sampling conducted in these situations must be viewed with due caution. In the initial exploratory phase, "flow-through" wells 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/bentonite seals or semi-permanent packers must be used.

For this exploratory phase, the Institute of Groundwater Studies, University of the Orange Free State, makes use of an ingenious method. They use an EC cell on a long cable in conjunction with a syringe sampler. The EC probe is lowered down the borehole and when an anomaly is detected, a syringe sample is collected. (F. Hodgson personal communication, 1991).

15.5 REFERENCES

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.

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 on the projects 75-84.02 and PW 86-038. DVGW-Forschungsstelle am Engler-Bunte-Institut, Universität Karlsruhe.

Rödelsperger, M.U. Rohmann and F. Frimmel 1991 A stationary packer system for layerwise groundwater sampling in monitoring wells - technique and results, Wat. Sci. Tech. 23, Kyoto, pp. 545-553.

UNESCO 1972 Ground-water studies, The UNESCO Press, Paris.

CHAPTER 16

PROTECTIVE CLOTHING

The amount of protection required by a sampler depends upon the nature of the site being sampled and the physical, chemical and biological properties of the waste itself. In many cases the individual waste products are relatively harmless but when combined react to produce hazardous by-products. The Machinery and Occupational Safety Act (MOS ACT) of 1983 (ACT No 6 of 1983) 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, then take appropriate action. This should be done on the pilot sampling run and potential hazards noted.

In South Africa waste disposal sites are divided into three classes, namely:

Class I - A containment site for the disposal of "special waste" (Group I waste). This class site requires an impermeable membrane or a relative impermeable strata that will efficiently contain both the waste and the leachate in the site or in the immediate surroundings thereof.

Class II - A site for the disposal of "general waste" (Group II waste). This site is known to emit leachate very slowly and continuously. Because of this an unsaturated zone is required under the site that can act as a biological filter that will allow air oxidation to decompose the leachate.

Class III- A site for the disposal of waste with an insignificant pollution potential (i.e. building material). This site is usually in hydraulic continuity with the groundwater and will emit any leachate that is formed in the site.

Thus if sampling groundwater at a Class I site, it is essential to wear personal protection equipment (PPE). At a Class II site PPE should be worn and at a Class III site do not be surprised to find that the explosimeter indicates 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. The MOS Act (GSR.2) stipulates that personnel are made aware of the potential hazards and the need for precautions.

Various types of safety equipment are recommended by the South African Protection Equipment Manufactures Association (SAPEMA) and are approved by various SABS codes. Contact SAPEMA at Johannesburg Chambers of Commerce and Industry, Private Bag 34, Auckland Park, 2006, Republic of South Africa and obtain the relevant information. Then acquire the proper equipment and appropriate training.

NOTE: CONTACT LENSES should NOT be worn at any site as they tend to concentrate organic materials around the eyes and soft plastic lenses can absorb chemicals directly. It is difficult to remove contact lenses quickly in an emergency especially if wearing protective clothing. It is better to wear spectacle adaptors or goggles. The MOS Act requires that appropriate PPE be worn by all personnel at a hazardous site.

CHAPTER 17

DECONTAMINATION

17.1 INTRODUCTION

Collecting groundwater quality samples is expensive in terms of both time and money. Obtaining erroneous results through cross-contaminating boreholes is unforgiveable. Following a few simple rules as set out in section 17.2 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.

17.2 BASIC DECONTAMINATION ROUTINE

These 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 17.3 must be followed.

Furthermore, if analysing for trace elements, especially trace organic compounds which are measured at parts per 10^{-9} or 10^{-12}, this procedure might be inadequate.

1. Start sampling at the borehole with the LOWEST concentration of chemicals and end up at the borehole with the HIGHEST concentration of chemicals.

2. 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.

3. Dispose of the purged water safely so that cross-contamination will not occur.

4. 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.

5. Use sampling equipment that is easy to clean, pumps that can easily be disassembled.

17.3 DECONTAMINATION AT SENSITIVE SITES

The American Society for Testing and Materials currently sponsors two sub-committees within Committee D18 on Soil and Rock. These subcommittees, D18.14, Waste Management and D18.21, Ground Water and Vadose Zone Monitoring, are developing decontamination standards for equipment used at hazardous waste sites. The Waste Management Subcommittee formed a task group (D18.14.01), charged with the responsibility to develop standard practices or guides for the decontamination of equipment used at hazardous waste sites (Mickam *et al.*, 1989).

When these procedures are published, they must replace the procedure described below.

17.3.1 MATERIALS

HARDWARE

- Washtubs, plastic or metal buckets and drums
- Drums for water supply
- Plastic sheeting
- Large plastic bags - clean unused fertilizer bags are suitable
- Water sprays - pesticide pressure sprayers are suitable
- Long-handled brushes
- Masking tape

CONSUMABLES

- Acid-resistant gloves and overalls
- Tap-water
- Phosphate-free detergent (for example Contrad^{R} which is available in South Africa)
- Standard pesticide-free cleaning solvent (for example isopropanol, acetone, hexane or methanol)
- 10 % (v/v) Nitric acid
- Deionised water

17.3.2 PROCEDURE

- Rinse with 5 % (v/v) solution of Contrad^{R} to remove gross contamination and particles;
- Rinse with tap-water to remove detergent;
- Rinse with solvent to remove absorbed organic contaminants;
- Rinse with acid solution to remove adsorbed inorganic contaminants;
- Rinse with deionised water to remove rinse solutions;
- Air-dry the equipment. Do not dry with towels which will reintroduce contamination.
- Seal in plastic bag and label accordingly.
- Dispose of the contaminated rinse water, rinse acid and rinse solvent in a pre-arranged site so as not to cause contamination.

Take due safety precautions when using the above procedure, as the acid rinse and the solvent rinse are hazardous materials. Collect a sample of the final rinse water and submit this to the analytical laboratory. This is your Field Blank (Chapter 6 pp 6-2).

17.4 REFERENCE

Mickam, J.T., R. Bellandi and E.C. Tifft 1989 Equipment decontamination procedures for ground water and vadose zone monitoring programs: Status and prospects. Ground Water Monitoring Review, Worthington, Ohio.

CHAPTER 18

SAMPLING OF SPRINGS AND SEEPS

18.1 SAMPLING SPRINGS

The sampling of a spring is straightforward because there is no need to purge. Be very careful not to allow cross-contamination. The best way to reduce cross-contamination is to use the borehole sampling pump and put it in the flowing water as close to the spring outlet as possible. Measure and record field parameters in the usual way. Rinse sample bottles and caps three times in the spring water, at a point as close as possible to the source and collect the sample.

18.2 SAMPLING SEEPS

Dig out seeps, let them flow until the water runs clear and sample as a spring. If necessary, install a well screen in the middle of the seep, develop it, and return the following day when the water has cleared. 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. If possible, sample seeps after a wet period.

CHAPTER 19

DRINKING-WATER QUALITY CRITERIA

(from Pieterse, 1989)

SABS SPECIFICATION FOR WATER FOR DOMESTIC SUPPLIES (SABS, 1984).

Determinand	Unit	Recommended maximum limit	Maximum allowable limit
Colour	mg/ℓ Pt	20	NS
Odour and taste	Shall not be objectionable		
Turbidity	NTU	1	5
pH	pH unit	6-9	5.5-9.5
Conductivity	mS/m	70	300
Macro-determinands	**mg/ℓ**		
Hardness, total	$CaCO_3$	20-500	650
Magnesium	Mg	70	100
Sodium	Na	100	400
Chloride	Cl	250	600
Sulphate	SO_4	200	600
Nitrate and Nitrite	N	6	10
Fluoride	F	1	1.5
Zinc	Zn	1	5
Micro-determinands	**µg/ℓ**		
Arsenic	As	100	500
Cadmium	Cd	10	20
Copper	Cu	500	1 000
Cyanide	CN	200	500
Iron	Fe	100	1 000
Lead	Pb	50	100
Manganese	Mn	50	1 000
Mercury	Hg	5	10
Phenolic compounds	Phenol	5	10
Selenium	Se	20	50
Bacteriological requirements			
Standard plate count	per 1 mℓ	100	NS
Total coliform	per 100 mℓ	0	5
Faecal coliform	per 100 mℓ	0	0
Radio-activity	If present shall be within the limits laid down by the International Commission for Radiological Protection		

NS = Not specified
NTU = Nephelometric turbidity units

19.2 REFERENCES

Aucamp, P.J. and F.S. Vivier 1987 A novel approach to water quality criteria in South Africa. Paper presented at Symposium Water 2000, IWSA, Nice.

Kempster, P.L. and R. Smith 1985 Proposed aesthetic/physical and inorganic drinking water criteria for the Republic of South Africa. Research Report (628), National Institute for Water Research, CSIR, South Africa.

Pieterse, M.J. 1989 Drinking-water quality criteria with special reference to the South African experience. Water SA 15 (3), Water Research Commission, South Africa.

SABS 1984 South African Bureau of Standards: Specification for water for domestic supplies. SABS 24101984, Pretoria.

PROPOSED DRINKING-WATER CRITERIA UNDER CONSIDERATION FOR APPLICATION IN SOUTH AFRICA (KEMPSTER AND SMITH, 1985; AUCAMP AND VIVIER, 1987).

Determinand	Unit	A	B	C
Physical and organoleptical				
Colour	mg/ℓ Pt	20	—	—
Conductivity	mS/m (25°C)	70	300	400
DOC	mg/ℓ C	5	10	20
Dissolved oxygen	% Sat	70	30	10
Odour	TON	1	3	10
pH	pH unit	6.0–9.0	5.5–9.5	<4.0 or >11.0
Taste	TTN	1	3	10
Temperature	°C	<25	<30	<40
Turbidity	NTU	1	5	10
Microbiological				
Standard plate count	per 1 ml	<100	1 000	10 000
Total coliform	per 100 ml	0	5	100
Faecal coliform	per 100 ml	0	1	10
Clostridium perfringens	per 100 ml	0	10	100
Coliphages	per 100 ml	0	10	100
Enteric viruses	per 10 ℓ	0	1	10
Macro-elements	µg/ℓ			
Antimony	Sb	50	100	200
Arsenic	As	100	500	600
Beryllium	Be	2	5	10
Bismuth	Bi	250	500	1 000
Cadmium	Cd	10	20	40
Chromium	Cr	100	200	400
Cobalt	Co	250	500	1 000
Cyanide	CN	200	300	600
Gold	Au	2	5	10
Lead	Pb	50	100	200
Mercury	Hg	5	10	20
Molybdenum	Mo	50	100	200
Nickel	Ni	250	500	1 000
Selenium	Se	80	50	100
Silver	Ag	20	50	100
Tellurium	Te	2	5	10
Thallium	Tl	5	10	20
Tin	Sn	100	200	400
Titanium	Ti	100	500	1 000
Tungsten	W	100	500	1 000
Vanadium	V	250	500	1 000

A = Recommended limit (maximum limit for no risk)
B = Maximum permissible limit (maximum limit for insignificant risk)
C = Crisis limit (maximum limit for low risk)
TON = Threshold odour number
TTN = Threshold taste number
NTU = Nephelometric turbidity units

PROPOSED DRINKING-WATER CRITERIA UNDER CONSIDERATION FOR APPLICATION IN SOUTH AFRICA (KEMPSTER AND SMITH, 1985; AUCAMP AND VIVIER, 1987)

Determinand	Unit	A	B	C
Macro-elements	mg/ℓ			
Aluminium	Al	0.15	0.5	1.0
Ammonia	N	1.0	2.0	4.0
Barium	Ba	0.5	1.0	2.0
Boron	B	0.5	2.0	4.0
Bromide	Br	1.0	3.0	6.0
Calcium	Ca	150	200	400
Cerium	Ce	<0	2.0	4.0
Chloride	Cl	250	600	1 200
Copper	Cu	0.5	1.0	2.0
Fluoride	F	1.0	1.5	3.0
Hardness	$CaCO_3$	20-300	650	1 300
Iodide	I	0.5	1.0	2.0
Iron	Fe	0.1	1.0	2.0
Lithium	Li	2.5	5.0	10.0
Magnesium	Mg	70	100	200
Manganese	Mn	0.05	1.0	2.0
Nitrate	N	6.0	10.0	20.0
Potassium	K	200	400	800
Sodium	Na	100	400	800
Sulphate	SO_4	200	600	1 200
Uranium	U	1	4	8
Zinc	Zn	1	5	10

A = Recommended limit (maximum limit for no risk)
B = Maximum permissible limit (maximum limit for insignificant risk)
C = Crisis limit (maximum limit for low risk)

CHAPTER 20

ABBREVIATIONS

Throughout the text symbols for the elements are used rather than the written name. Only where necessary is the name used.

COD	-	Chemical Oxygen Demand
DNAPL	-	Dense non-aqueous phase liquids
DO	-	Dissolved Oxygen
DOC	-	Dissolved Organic Carbon
DOX	-	Dissolved Organic Halogens(x)
EC	-	Electrical Conductivity
Eh	-	Redox potential
LNAPL	-	Light Non-aqueous phase liquids
m	-	metres
mg/L	-	milligrams per Litre
mm	-	millimetres
mS/m	-	milli-Siemens per metre
mV	-	millivolts
NVOC	-	Non-Volatile Organic Compounds
pH	-	pH
TDS	-	Total Dissolved Solids
THMs	-	Trihalomethanes
TOC	-	Total Organic Carbon
TOX	-	Total Organic Halogens (x)
VOC	-	Volatile Organic compounds

CHAPTER 21

SUGGESTED READING

American Society for Testing Materials 1969 Manual on Water, ASTM Special Technical Publications, (442).

APHA 1989 Standard methods for the examination of water and wastewater 17th Edition. Washington, D.C., Am. Public Health Assoc.

Canter, L.W., R.C. Knox and D.M. Fairchild 1987 Ground water quality protection. Lewis Publishers, Michigan.

Everett, G.L. 1980 Groundwater monitoring. Genium Publishing Corporation, Schenectady.

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.

Lloyd, J.W. and J.A. Heathcote 1985 Natural inorganic hydrochemistry in relation to groundwater. Clarendon Press, Oxford.

Schalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby and J. Fryberger 1981 Manual of ground-water sampling procedures. National Water Well Association, Worthington, Ohio.

Wisconsin Department of Natural Resources 1987 Groundwater sampling procedure field manual, Publ. WR-168-87. P.O. Box 7921, Madison, WI53707.

Wood, W.W. 1981 Guidelines for collection and field analysis of ground-water samples for selected unstable constituents. Techniques of Water Resources Investigation, Chapter 2, US Geological Survey.