

# QA Issues for Site Hydrochemical Data Used for Groundwater Evolution Models

June 1999

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1999

*QA Issues for Site Hydrochemical Data Used for  
Groundwater Evolution Models*

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*Abstract*

Groundwater data used for modelling site or repository evolution need to be assessed for their quality and whether they are “fit for purpose”, prior to utilization. This report discuss factors and issues which impinge upon the quality of such data. It is recommended that geochemical modelleres :

- are aware of how groundwater samples were collected, whether during drilling, during hydraulic testing, or thereafter, by in-situ measurement, pumped from boreholes, or by pressurised sampler ;
- are aware of what procedures (if any) were used to “correct” samples for drill fluid contamination and what errors were associated with those methods ;
- are aware of whether samples were subject to de-pressurisation during sampling, and whether geochemical modelling techniques were applied to correct the compositions of samples for that process ;
- request different measures of redox activity (e.g., electrode measurements of Eh, concentrations of different redox-sensitive aqueous species) to be applied to key groundwater samples to investigate the extent of redox equilibrium ;
- are aware of how groundwater samples were filtered and preserved for off-site analysis ;
- ensure that adequate methods of groundwater filtration ( $< 0.1 \mu m$ ) and chemical analysis are applied to ensure accurate and reproducible analyses for dissolved aluminum at low levels of concentration (generally less than 0.2 mg/L) ;
- are aware of elemental errors and detection limits in chemical analysis of groundwater samples and assess the quality of groundwater analyses via ion exchange balances and via a comparison of measured and calculated values for total dissolved solids contents.
- ensure that detailed mineralogical analysis is carried out on rock samples from locations where key groundwater samples have been extracted.

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## 地下水水質形成モデルで求められる地下水データの品質保証項目

(研究報告)

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### 要 旨

地下水水質形成のモデル化の対象となるサイトや処分場の変遷過程を評価するために地下水データを用いる場合、データを用いる前に、データの品質や目的にあったデータであるかどうかについての評価を行う必要がある。本報告書では、データの品質保証に係わる事項・内容について整理した。その結果、地下水地球化学に関するモデル化を行う上では、以下の点に留意することが必要であると考えた。

- ・ どの様にして地下水試料がサンプリングされたか（試錐孔掘削中にサンプリングされた地下水か、水理試験の間にサンプリングされた地下水か、原位置での測定値か、試錐孔からポンプで汲み上げられた地下水か、原位置での圧力状態を保ったままサンプリングされた地下水か）。
- ・ 掘削水の影響等を受けていない地下水試料をどの様にしてサンプリングしたのか。また、その手法に伴う地下水試料への影響（誤差）は、どの程度なのか。
- ・ 地下水サンプリングの間に脱ガスの影響を受けていないか。もし脱ガスの影響を受けているならば、もとの状態の（正確な）地下水組成を推定するため、地球化学モデルによる補正がなされているか。
- ・ 地下水の酸化還元状態の非平衡の度合いを把握するため、キーとなるサンプルに対して、異なる手法（例えば、電極による Eh の測定や酸化還元反応に鋭敏な化学種濃度の測定等）による酸化還元状態の調査が行われているか。
- ・ 地下水試料の濾過方法はどの様にして行われたか。また、室内での水質分析のために、地下水試料をどの様に保存していたか。
- ・ 低濃度である溶存アルミニウム（通常、0.2 mg/L 未満）の測定にあたり、精度良く、再現性のあるデータを得るため、地下水試料の濾過（ $< 0.1 \mu\text{m}$ ）や化学分析について、十分信頼できる方法が採用されているか。
- ・ 地下水試料の化学分析における誤差や検出限界はどの程度なのか。また、測定値に誤りが無いかどうかを確かめるため、電荷バランスのチェックや全溶解成分に関する測定値と計算値の比較等を行っているか。
- ・ キーとなる地下水試料が採取された場所での岩石試料に対して、詳細な鉱物学的分析が行われているか。

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# 1 Introduction

The interpretation of site geochemical data (groundwaters and rocks) depends upon the type, quantity, and quality of the data collected. It is highly likely that such interpretations will at best be vague, and at worst misleading, if the supporting field data are unreliable. In turn, the reliability of the field data is determined by the procedures followed to:

- ▲ obtain 'representative' groundwater samples, *i.e.* those that are unaffected by perturbations resulting from drilling and sampling,
- ▲ obtain a complete set of mineralogical samples from drill cuttings/cores, fracture fillings and fracture surfaces, and from unaltered host rocks,
- ▲ measure, in the field and/or laboratory, chemical parameters in the sampled groundwaters, and,
- ▲ process the measured data, for example to correct for the effects of degassing during sample collection, on *in situ* pH.

Issues of sample contamination during collection, incorrect preservation and storage procedures, and inappropriate analytical techniques can contribute additional uncertainties to the quality of the data. The spatial/temporal coverage of sampling/monitoring also impinges upon whether the data are suitable for the purpose of accurately describing the geochemical characteristics of the groundwater system.

This report addresses criteria by which JNC geochemical modellers can assess the quality of hydrochemical data collected at field sites such as Kamaishi, Tono, and Mobarra. These criteria address whether the data:

- ▲ are relevant and suitable for the purpose of accurately characterising groundwater chemistry and site mineralogy,
- ▲ are adequate in terms of the depth, spatial and temporal coverage of groundwater and mineralogical samples,
- ▲ are representative of sub-surface conditions, and
- ▲ reflect potential sources of uncertainty and that these are adequately represented in reported values.



## 2 Groundwater Sampling Methods

Groundwater samples may be obtained from surface springs, underground excavations (mines, underground laboratories), or from boreholes. It is important to establish the principal source of the groundwater sample to be able to evaluate its suitability for use in geochemical modelling. Groundwaters may be sampled from boreholes:

- ▲ during drilling;
- ▲ during hydraulic testing of the borehole;
- ▲ post-borehole completion.

These sample types are discussed in more detail, below.

### 2.1 Sampling during drilling

Samples taken during drilling are analysed for a restricted suite of parameters (normally tracer concentration, specific gravity, alkalinity, pH, electrical conductivity plus some major anionic and cationic species).

These groundwater samples are not representative of the real groundwater composition due to the very high level of contamination by the drilling fluid. Nonetheless, these samples have some value since gross changes in any of the measured parameters may indicate that the borehole has intersected a water-bearing zone or fracture. In addition, these samples may also be analysed, for safety reasons, to detect the presence of gases or other flammable or explosive hydrocarbons.

Once the drilling work has been completed but prior to taking water samples for detailed analysis, the borehole is flushed (cleaned). The aim of flushing is to remove any drilling fluid from the borehole, nearby rock matrix and fractures and to return the hydrochemical conditions to the natural state.

The entire borehole may be flushed using pumps or bailers but it is more common to focus on individual hydraulically-active flowing zones or fractures. These zones are isolated from the rest of the borehole by a straddle packer assembly. The degree of contamination of the groundwater by the drilling fluid is quantified using the tracer concentration in the water. As pumping continues, the concentration of tracer will decrease. Water is not actually taken for sampling until the tracer concentration is sufficiently low; usually less than 1 %. An example of the decrease in tracer concentration with continued pumping from the El Berrocal study in Spain is given in Figure 2.1.

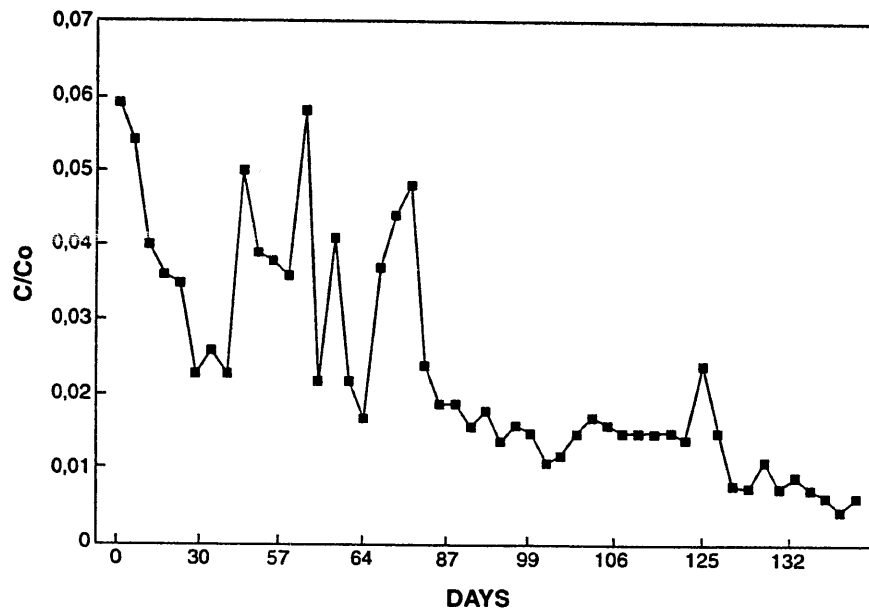


Figure 2.1: Decrease in tracer concentration (KBr) when flushing a borehole at El Berrocal (From Miller, 1995).

Table 2.1: Fluid volumes extracted by Nagra to achieve clean waters.

Drilling fluid	Water volume to be extracted
<i>If no drilling fluid lost during drilling, then one drill string volume should be extracted, plus:</i>	
Deionised water	5 to 10 times the volume of the test interval
Fresh water	10 to 20 times the volume of the test interval
Groundwater	10 to 20 times the volume of the test interval
Clay-freshwater	30 to 70 times the volume of the test interval
Clay-saltwater	40 to 200 times the volume of the test interval
<i>If significant drilling fluid lost during drilling these additional volumes must be extracted:</i>	
Deionised water	3 to 4 times the volume lost
Freshwater	4 to 8 times the volume lost
Clay+freshwater	5 to 10 times the volume lost
Clay-saltwater	10 to 40 times the volume lost

Groundwater samples taken during drilling should not, in general, be used for geochemical modelling purposes.

## 2.2 Downhole analyses

Once the borehole has been drilled to the required depth and flushed, it is possible to lower downhole geochemical probes into the borehole to measure certain physico-chemical parameters *in situ*. This has the advantage over sampling at the surface that the water is under natural pressures and temperatures thus avoiding perturbations to the chemistry due to P, T changes that commonly occur during sampling. However, since most probes are used to obtain a continuous geochemical profile down the borehole, they must be used in open holes which may mean that groundwaters with contrasting chemistry, originating from different flowing horizons, may mix in the borehole to give spurious geochemical results. It is possible, with some smaller designs of downhole probe, to avoid this problem by locating the probe between a double packer assembly sited across a flowing zone/fracture.

A number of geochemical probes have been designed. A commonly used probe is named IDRONAUT which was used in the El Berrocal project. This probe can measure simultaneously temperature, pH, *Eh*, EC and O<sub>2</sub>. An example of a geochemical profile obtained in one of the El Berrocal boreholes using the IDRONAUT probe is given in Figure 2.2. The obvious change in *Eh* and O<sub>2</sub> occurring at around 130 m corresponds to a hydraulically-active fracture bringing less oxidising water to the borehole.

## 2.3 Surface sampling

In most cases, groundwaters are required from individual flowing zones or fractures and so these are isolated using a straddle packer assembly, rather than collecting groundwaters from open boreholes, thus avoiding the risk of groundwaters mixing.

In some cases, the head in a packed-off section is sufficiently high that artesian free-flow to the surface can occur via tubing connected to the packed-off section. However, in most cases, the heads are too low for this and groundwaters must be recovered by some mechanical method. Three main techniques are available: pumping, swabbing and air-lift, as shown in Figure 2.3. Pumping uses a pump located in the borehole or at the surface to drive (or suck) water from the packed-off section to the surface. Two types of pump are commonly used. The first is a submersible pump which sits in the water, in the borehole, and drives the water directly to the surface. The second is a peristaltic pump which is

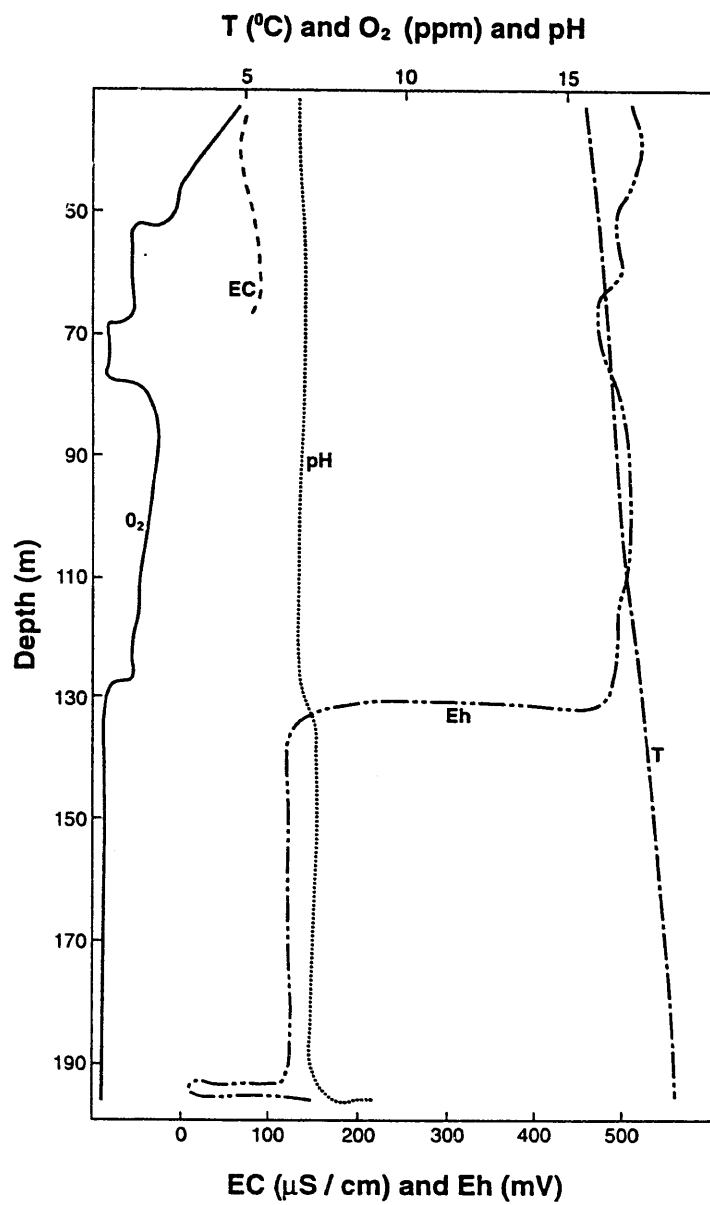


Figure 2.2: Example of a geochemical profile obtained using the downhole probe IDRONAUT. From Miller (1995).

usually located at the surface. Pumps have the disadvantage that they can fail if the water contains a high proportion of solids or is very viscous. For very deep boreholes with waters with a low head, it may be necessary to pump water considerable distances (may be up to 1 km vertically) to the surface and, in this situation, a powerful pump is required.

Swabbing involves lowering a swabbing bar with rubber swabbing cups into a hollow PVC tubing (or possible the drill string). When the swabbing tool is lowered beneath the water level, fluid flows over the swabbing assembly through simple one-way valves. When the equipment is then raised, these valves close and the fluid column above the cups is lifted to the surface. Unlike pumps, swabbing tools can retrieve water with a high solid load and can be used to any depth. They are not, however, very efficient in inclined boreholes when water can spill from the cups.

Due to the high risk of contamination of the groundwater with the air (or other gas), and the fact that air-lift encourages degassing of the sample, water to be collected for high-quality analysis is not usually collected by air-lift. The technique is, therefore, usually reserved for sampling during drilling.

Using any of these methods, groundwater samples can be collected at the surface via tubing connected to the packed-off section once this section has been adequately flushed. Where groundwaters are pumped, care must be taken not to use too high flow rates since this can induce leakage of groundwater at the packer/rock interface or through the rock mass. If the packer assembly contains sufficient pressure monitoring devices, then the effect of sampling can be assessed.

To avoid contamination of the groundwater by air, the tubing is sealed at the sampling head. This head is generally equipped with valves for regulating the groundwater flow rate; an outlet for groundwater collection; and a flow-through cell with sockets for on-line analyses of various physico-chemical parameters such as *Eh*, pH, T, pO<sub>2</sub> and EC. A schematic diagram of a flow through cell is shown in Figure 2.4.

## 2.4 Downhole sampling

In zones with very low hydraulic conductivity or low flow rate, it may be impossible to obtain sufficient volumes of water via surface sampling because of the need to fill the volume of tubing connecting the packed-off section to the surface (the so-called 'dead volume'). In such cases, it is convenient to collect the groundwater downhole at the packer assembly itself. Two types of device are normally used for such sampling: an evacuated single-valve sampler or a

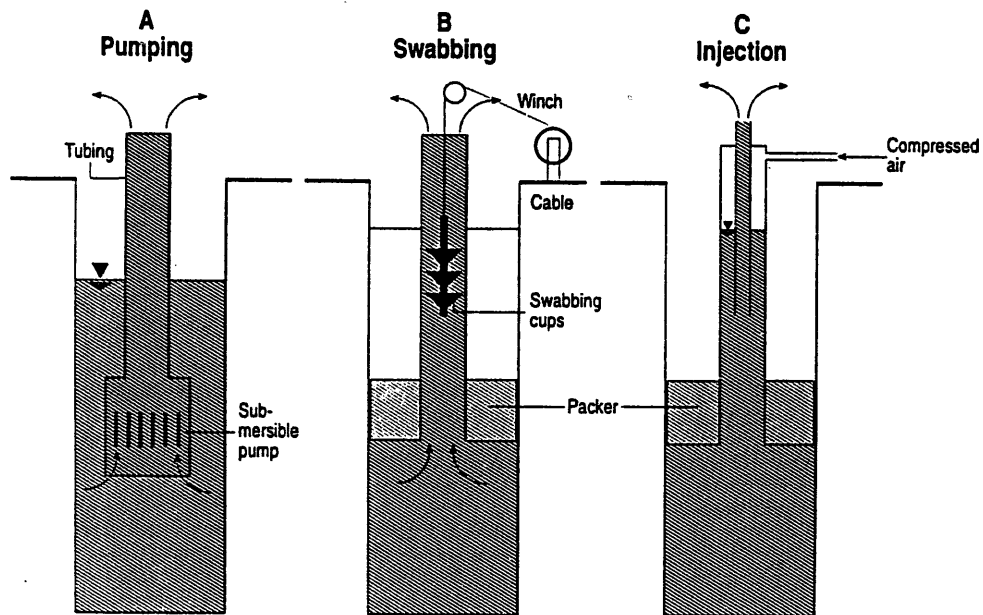


Figure 2.3: Methods for lifting groundwater samples to the surface. From Kupfer *et al.* (1989).

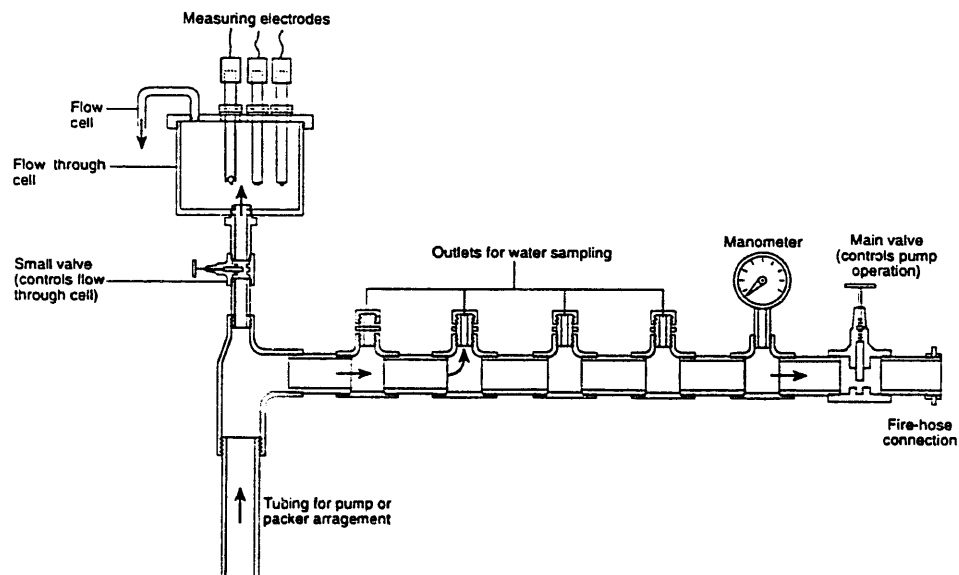


Figure 2.4: Schematic diagram of a sampling head with a flow through cell fitted. From Gautschi and Scholtis (1989).

flow through sampler with inlet and outlet valves.

A major disadvantage of downhole sampling devices is the limited sample volume that can be collected at each operation, often as little as 1 litre at a time. Modified downhole samplers such as the Large Volume Sampler (LVS) used at the Sellafield site (U.K.) can collect a fixed volume of 5 litres but this is about the maximum volume that can be collected.

All samples collected at the surface, or collected at depth and transferred at the surface to standard containers, will suffer from degassing due to the lower pressure at the surface compared to at depth. The extent of this degassing is likely to be variable and unknown.

To avoid perturbations to the aqueous chemistry due to degassing, or to analyse the dissolved gases themselves, downhole pressurised sampling devices have been designed. These samplers collect the groundwater at the packer assembly, at ambient pressures, and maintain that pressure as it is brought to the surface thus containing the sample as a single phase. These devices are designed so that the sample can be transferred to pressurised sample 'bombs' without degassing or contact with the atmosphere.

Pressurised samples collected at depth are the least disturbed, nearest to natural state samples that current technology can allow. However, they usually are restricted by the very small volumes of groundwater they can contain. As an example, the Single-Phase Reservoir Sampler (SRS) used at Sellafield by Nirex has a fixed volume of only 0.6 litre.

## 2.5 Post-completion sampling

As mentioned earlier, after drilling, the borehole will be flushed before groundwaters are collected for analysis. The degree of contamination by drilling fluids is monitored by the decrease in concentration of the drilling tracer.

However, low tracer concentrations do not mean that the measured groundwater compositions necessarily reflect the true, natural groundwater state since it can take considerable time for the hydrochemical regime to return to normal after the drilling-induced perturbations. This is particularly the case for the trace element concentrations, such as uranium, because drilling fluids are invariably oxidising and, consequently, will undergo dissolution and redox reactions with chemically reduced phases in the rock. This results in perturbed hydrochemical signatures, usually with elevated trace element concentrations. As pumping continues and redox conditions return to the natural state, dissolution and redox reactions will cease and trace element concentrations fall to

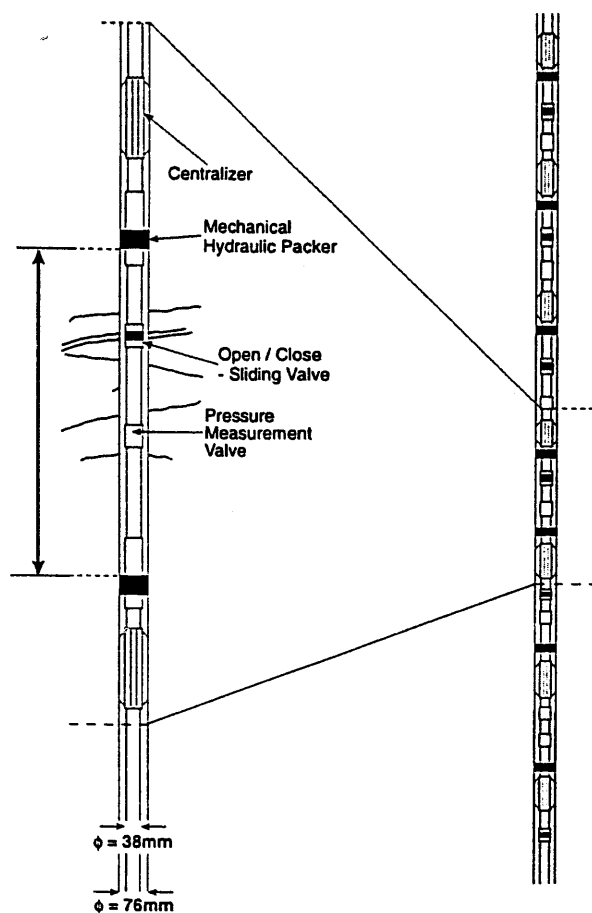


Figure 2.5: Westbay completion at the Canadian URL (From Davison, 1985).

normal levels. This may take much longer than is required to pump out the drilling fluid.

If logistical constraints allow, it is very instructive to monitor the groundwater compositions in the borehole over a long period of time after drilling has stopped. This is best achieved by isolating separately all of the individual flowing zones that intersect the borehole to avoid mixing of groundwaters with different compositions. Such a borehole 'completion' is exemplified by the Westbay system (Figure 2.5), such as the one used at the Canadian Underground Research Laboratory, URL, (Davison, 1985). Completing a borehole is also a valuable exercise from a hydrogeological perspective since it allows hydraulic parameters of the system, such as heads (pressures), to return to their natural state and be measured.



## 2.6 Summary

Most reliance should be placed upon groundwater samples extracted either during hydraulic testing or in the post-completion phase of the borehole. Groundwater samples extracted during drilling operations or in the immediate post-drilling period are likely to be suspect from a contamination perspective. Modellers should question samples obtained using techniques which involve sample de-pressurisation unless other consistency checks (*e.g.* geochemical modelling, see below) prove otherwise.

### 3 Sample Intervals and Locations

Different procedures for groundwater sampling are adopted for fractured rocks in contrast to those used in porous/permeable rocks since, in the former type, groundwater flow is restricted to specific fractures while, in the latter type, groundwater flow may occur throughout an entire lithological formation (aquifer).

In fractured rocks (crystalline or fractured argillaceous rocks), groundwater sampling is only worthwhile at hydraulically-active fracture zones since the hydraulic conductivity of the rock mass is too low for advective water movement. The locations of hydraulically-active fractures may be determined using a combination of sources of information, for example:

- ▲ location of open fractures identified in the core,
- ▲ down-hole, geophysical logs (e.g. caliper, gamma, acoustic televiewer),
- ▲ down-hole geochemical probe profiles,
- ▲ hydrogeological test data (e.g. slug tests, cross-hole tests), and
- ▲ drilling records (e.g. volume of drilling fluid lost).

Once the locations of the hydraulically-active fractures are identified, each fracture is isolated using the straddle packer assembly, with a packer spacing sufficiently wide to stretch across the flowing zone. In many cases, this zone may be the width of a single fracture (around 1 cm) but, in other cases, the flowing zone may comprise a suite of closely spaced, interconnected fractures extending over a distance of several metres.

In porous/permeable rocks, it may not be possible to use a straddle packer assembly to isolate the entire thickness of an aquifer horizon. In such cases, the straddle packer may be moved incrementally up or down the entire borehole depth and samples collected at each interval. The straddle packer spacing must be chosen to suit the local conditions but is likely to be in the range of 1 to 10 m.

A common concern with this type of sampling (particularly in hard fractured rocks), is the representativeness of these samples of pore waters in the rock matrix. Since geological formations of interest to waste disposal are by necessity of low permeability, locations for sampling groundwater are so-called 'flowing features', which are the more permeable zones within the rock mass. It may be impossible to obtain sufficient volume of groundwater from less-permeable sections for requirements of chemical analysis. The dilemma which faces the geochemist is how representative are the chemical compositions of groundwater

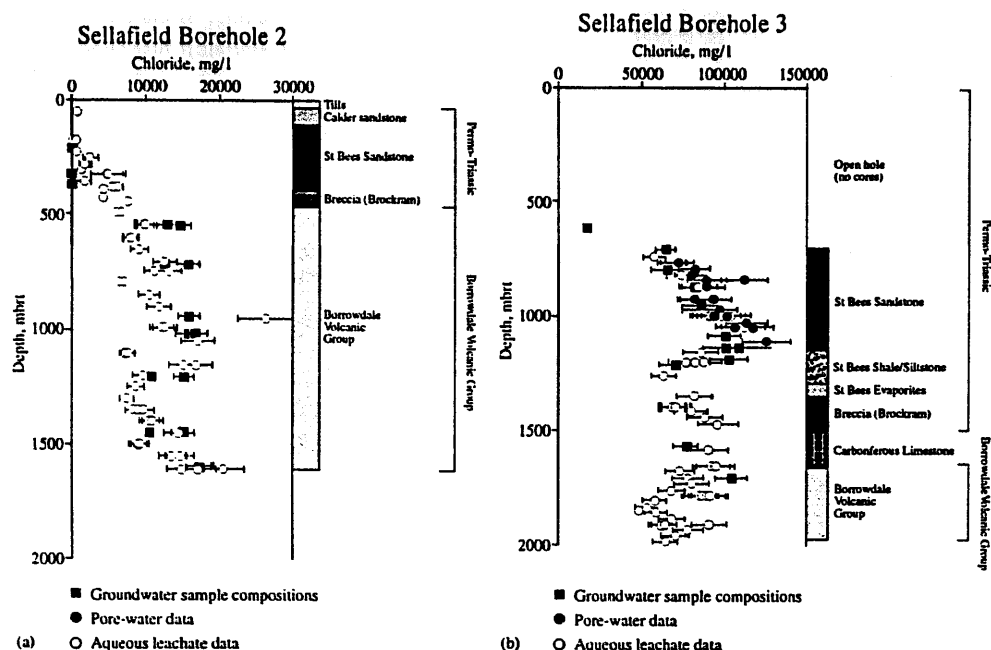


Figure 3.1: Profiles of chloride concentrations in two boreholes at Sellafield, U.K., showing data obtained by borehole sampling, pore fluid centrifugation and crushed core leaching. From Bath *et al.* (1996).

samples obtained from these more permeable zones, of the rock mass as a whole? It is conceivable that the borehole zones which flow more freely with groundwater do not contain groundwater which has a composition typical of the bulk rock mass.

U.K. Nirex Ltd. has tried to address this issue during site characterisation activities at Sellafield by analysing pore fluids extracted from the drillcore (Bath *et al.*, 1996). Pore fluids have been extracted from drillcore in the laboratory, either by centrifugation for more permeable rock types such as the Sherwood Sandstone Group, or by leaching of dried, crushed drillcore using deionised water for less permeable rocks. The chloride concentrations of the pore solutions are calculated from the composition of the leachate solution and the water content of the preserved saturated drillcore. Correction of the data for drill-fluid contamination is achieved using the observed concentration of lithium (used as a drill-fluid tracer at Sellafield) in the pore water and an appropriate drill-fluid concentration. This approach is believed to be accurate for conservative solutes such as chloride, but may be less relevant for solutes subject to water-rock reaction during the leaching process. Figure 3.1 compares data for 2 boreholes at Sellafield using three methods of obtaining analytical data. Nirex seem satisfied that data derived by the three methods produce similar results, suggesting that groundwater samples obtained during borehole testing are representative of pore fluids in the rock matrix.

### **3.1 Summary**

From a geochemical modelling perspective, it must be realised that it is not always possible to be able to sample groundwaters at every desirable location in low-permeability rocks, because of the lack of flowing zones. However, sampling immediately above and below lithological or structural features is highly desirable to be able to identify potentially different zones in the groundwater regime. Long-term time-series monitoring using borehole completions is also very important to be able to establish the stability of groundwater compositions in specific geological zones.

## 4 Drill Fluid Contamination

Drilling tracers are often added to the drilling fluid to allow the degree of contamination of the groundwater samples by the drilling fluid to be quantified. While simple in concept, in practice there are a number of drawbacks with using tracers and, to overcome these, there are a number of requirements that the ideal tracer should meet:

- ▲ it should be quick, easy and inexpensive to detect using on-site measurement techniques,
- ▲ it should be non-toxic and non-radioactive,
- ▲ it should be exotic to the hydrochemical system, with no significant background concentration, and
- ▲ it should be conservative in the groundwater, *e.g.* it should not sorb onto the rock or mineral surfaces to any great extent.

Due to the variable nature of rock-water systems, no tracer is ideal for all situations and careful consideration must be given to choosing which tracer to use at each drilling site. Many different tracers have been used in various studies, including sodium fluorescein (uranine), m-TFMBA (meta-trifluoromethylbenzoic acid), lithium, iodine and bromine. The tracers are usually added to the drilling fluid as a dissolved concentrate in sufficient amounts to reach a detectable concentration in the returned drilling fluid.

The contamination by drilling fluid can also be checked independently by measurement of the tritium ( $^3\text{H}$ ) content. Since tritium has a very short half life (12.4 years) compared to the residence times of most groundwaters, and occurred in infiltrating waters only after the first thermonuclear explosions, it is possible to use tritium concentrations as a tracer. However, tritium measurement requires off-site laboratory mass spectrometric analysis and is, therefore, less than ideal.

Tracers can also enter core samples and can be detected in the laboratory if porewaters are abstracted. The concentration of the tracer in the porewater gives an indication of the representativity of the porewater compositions.

For both groundwater and porewater samples, the composition of 'natural' water can be estimated using simple mixing equations given that the tracer concentration gives an estimate of the relative proportions of the drilling fluid and the natural water. A more detailed approach to calculating the 'true' composition of the groundwater from the composition of the contaminated sample

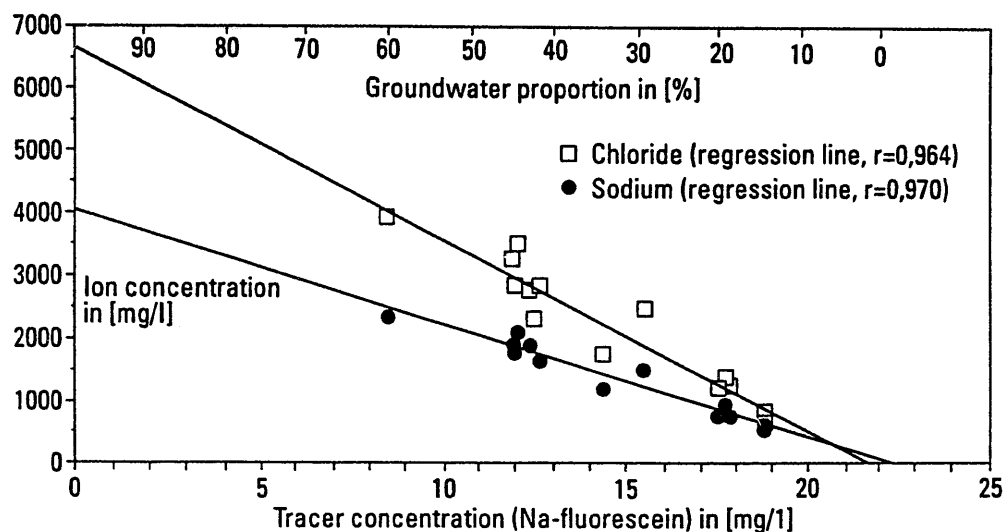


Figure 4.1: The calculation of the chemical composition of groundwater at 1326 m depth in the Bottstein borehole, Switzerland, using a linear regression method. Data are extrapolated to zero concentration of tracer to establish the composition of the groundwater uncontaminated by drill fluid. From Gautschi and Scholtis (1989).

uses linear regression calculations (*e.g.* Figure 4.1). Such an approach requires that a number of assumptions are fulfilled:

1. The drilling tracer is fully inert in the rock-water system;
2. The concentration of the tracer is zero in the uncontaminated groundwater;
3. The composition of the drilling water is known and constant;
4. only one compositionally distinct groundwater exists in the groundwater system;
5. The analytical results are accurate;
6. The sample is unmodified by the collection procedure; and
7. The compositional parameter is expressed as a concentration.

It is unlikely that all of these assumptions will be true in all cases and, consequently, the calculated compositions should be seen as approximations to the true groundwater composition. The last of these assumptions is true for most species (can be expressed as a concentration) but not for pH,  $Eh$ ,  $^{14}C$  and  $\delta^{13}C$ .

In practical terms of using groundwater analyses for quantitative modelling, some assessment or 'quality score' of each groundwater analysis needs to be

assigned, using the above criteria in order to identify good from poor samples. These quality scores should be based upon:

1. Whether the least squares fitting or estimation procedure has been employed or not.
2. How much tracer is present in the sample. The lower the content of tracer, the higher the quality score should be.
3. The number of samples used in the estimation procedure. The quality score should increase as the number of samples used to carry out the estimation increases.
4. The number of drilling fluid samples used in the estimation procedure. This parameter is only important if a drilling fluid correction is required.
5. The compositional difference between the drilling fluids and the contaminated groundwaters. This parameter is only important if no correction for drilling fluid contamination has been used. The error from the lack of correction then depends upon the tracer content of the contaminated groundwaters and the difference between the composition of these and the drilling fluid samples.
6. The reactivity of the chemical species concerned. Some species are less reactive than others in the drilling fluid–groundwater–rock system.

SKB have considered both 'manual' and computer based mathematical methods to assess groundwater quality (Laaksoharju *et al.*, 1993). Manual systems assess qualitative indicators of quality which may be difficult to assess mathematically and rely to a large part upon expert judgement. Unfortunately, there can be a large degree of subjectivity in this method so that different experts may place different 'scores' on the same data. Mathematical models are more rigorous and better documented so that reproducibility is high. However, this method tends to oversimplify the ranking process which leads to a loss of sensitivity. Also, there is a danger that computer-based methods become something of a 'black-box' which automatically process groundwater data.

Modellers should thus endeavour to ensure that groundwater compositions derived from hydrogeologists and chemical analysts receive some sort of quality score which reflects the sampling and analytical procedures. Model calculations should therefore only be carried out upon groundwater compositions with high quality scores.

## 5 Sample Depressurisation and pH, Redox Measurement

### 5.1 Sample depressurisation and pH

Pumping or lifting of groundwaters from depth in a borehole to the surface will result in a pressure change and exsolution or solution of gases. This is a particular problem for carbon dioxide. Since sub-surface partial pressures of CO<sub>2</sub> may be different from atmospheric, when the groundwater is returned to the surface, CO<sub>2</sub> will either escape (pH rises) or be absorbed (pH decreases). This will result in major changes to fluid chemistry (total inorganic carbon content, pH). The problem of CO<sub>2</sub> loss and absorption may be avoided by the use of pressurised borehole samplers or down-hole electrode measurements. Most down-hole hydrochemical measuring equipment has been developed with radioactive waste objectives in mind (*e.g.* Almen and Zellman, 1991). Experiments to compare measurement of pH and redox parameters at depth and on the surface have been conducted as part of the Swedish radioactive waste disposal programme (Wikberg *et al.*, 1987) which concluded that these parameters should be determined *in situ* wherever possible. However, such methods are more expensive than other techniques.

Where *in situ* measuring devices have not been employed, the problem of gas loss has been compensated for by the use of chemical modelling techniques (*e.g.* Pearson *et al.*, 1989). These methods rely upon the common occurrence of calcite as a mineral in rocks and the assumption of equilibrium between calcite and the *in situ* groundwater. Using a chemical analysis of the groundwater, CO<sub>2</sub> is numerically 'titrated' into the groundwater until equilibrium between calcite and the groundwater is achieved and pH is calculated accordingly. 'Reaction path' software such as PHREEQE (Parkhurst *et al.*, 1980) or EQ3/6 (Wolery, 1992) is commonly employed in this manner. Although the assumption of calcite-groundwater equilibrium is reasonable for many groundwaters, it cannot be applied to groundwaters where co-existence with calcite does not apply. For example, the assumption of equilibration of groundwaters with calcite may not be universally relevant in groundwaters at depth in basement 'crystalline' rocks where the principal source of carbonate is derived solely from atmospheric recharge. The progressive precipitation of calcite as groundwaters percolate to depth may mean that at some depth there will be insufficient carbonate available to precipitate calcite.



Table 5.1: Different redox levels indicated by different redox couples in groundwaters extracted from the Fox Hills aquifer, USA (from Hostettler, 1984). Concentrations in mmol/L.

	Medora Well	Hazen Well
$Eh$ , measured (mV)	-67	-92
pH, measured	8.83	8.60
$SO_4^{2-}$	2.29	0.031
$HS^-$	0.003	< 0.001
$Eh$ ( $SO_4^{2-}/HS^-$ ) [mV]	-320	> -315
$N_2$	0.93	0.78
$NH_4^+$	0.077	0.018
$Eh$ ( $N_2/NH_4^+$ ) [mV]	-334	-304
$HCO_3^-$	11.6	19.1
$CH_4$	0.0025	2.75
$Eh$ ( $HCO_3^-/CH_4$ ) [mV]	-357	-362

## 5.2 Redox measurement

The measurement of redox relies upon an assumption of homogeneous equilibrium between all redox species in an aqueous solution. Unfortunately, in natural waters, this is seldom the case and thus the assumption of a 'system  $Eh$ ' is a poor one. Redox reactions generally rely upon the breaking of strong covalent bonds involving aqueous species of elements such as carbon, nitrogen and sulphur and the breaking of these bonds is catalysed by microbial processes. As a consequence, these reactions are slow and irreversible, so that different redox couples may indicate different redox levels for the same water, *e.g.* data shown in Table 5.1. Models of aqueous speciation and solubility may require the adoption of different values of redox for different redox couples. For speciation and solubility calculations, it may be necessary to adopt redox values for the most chemically-similar redox couples to the radioelement of interest. This requires that various redox couples have been measured in a groundwater. It is important that the concentrations of as many redox couples as feasibly possible are determined in key groundwaters, in addition to the determination of  $Eh$  by platinum electrode. Redox couples which should be investigated include:  $SO_4^{2-}/HS^-$ ;  $N_2/NH_4^+$ ;  $NO_3^-/NO_2^-$ ;  $HCO_3^-/CH_4$ ;  $As^{III/IV}$ ;  $Fe^{II/III}$ .

In the field,  $Eh$  is usually measured using platinum and reference electrodes. However, a platinum electrode responds unsatisfactorily to most redox couples important in natural waters. In oxidising waters,  $Eh$  values measured by electrode rarely correspond to a specific redox couple. In reducing waters,  $Eh$

values may be of more relevance.

Like pH, it is important to measure *Eh in situ* rather than at the surface. However, in the borehole environment, redox measurements will be strongly affected by exposed steel or iron, *e.g.* from casing, drill pipes or packer strings. It is therefore advisable to keep such contamination to a minimum (by isolating sections of borehole using packers on a teflon-coated string) in order to derive meaningful redox measurements.

### 5.3 Summary

With regard to geochemical modelling, groundwaters where parameters such as pH, redox have been measured *in situ* should receive greatest attention as being the most representative of *in situ* conditions. Samples where these parameters have been measured remotely should be treated with some caution and be subjected to consistency tests using geochemical modelling. For example, do geochemical calculations of mineral saturation states accord with minerals observed *in situ*? Deviations from these observations may suggest that measured parameters such as pH and redox are inaccurate.

## 6 Sample Filtration and Preservation

After collection (by whatever method), groundwater samples should be filtered, and for components measured off-site, preserved for chemical analysis.

Filtration should in all cases be carried out to exclude particulate material  $< 0.45 \mu\text{m}$ , and for aluminium, manganese, and iron analysis,  $< 0.1 \mu\text{m}$ . Aluminium data for samples not filtered to  $< 0.1 \mu\text{m}$  should be treated with the utmost caution for purposes of geochemical modelling.

On-site analytical facilities will be project specific but it is normal to maintain some equipment to determine labile (unstable) parameters that are susceptible to change during extended periods for transport and storage such as pH, dissolved  $\text{O}_2$ , total and carbonate alkalinity, total inorganic and organic carbon, nitrite, nitrate, ammonia and  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ . In addition, major and some minor elemental concentrations may be determined if equipment is available. For example, at Aspö, Sweden, the field laboratory was equipped with an ion chromatograph, spectrophotometer, fluorimeter and titration equipment.

Groundwater samples may be collected for a wide range of off-site analyses such as dissolved components, isotopes, gases, microorganisms *etc.* The collection procedure and container preparation will be dependent on the requirements for specific analyses. In some cases, the groundwater may require some treatment to stabilise it for transport and storage. Common treatments are given in Table 6.1 based on information from the US EPA (1974).

The purpose of the different preservative agents is to stop reactions such as precipitation or sorption on to container walls that would cause a change in the apparent concentration of certain chemical species. The effects of adding the different preservatives to groundwaters are given in Table 6.2.

It should be noted that the flow rate and hydraulic parameters of the packed-off section provide a direct constraint on the rate at which groundwater can be collected. This is critical since a full suite of off-site analyses will require a number of separate aliquots of the groundwater to be collected from the packed-off sections; one aliquot for each laboratory and analytical procedure as a minimum. Furthermore, certain analytical methods require very large volumes of groundwater. As examples, analysis of oxygen and hydrogen isotopes on the groundwater itself requires around 1 litre of water; analysis of  $^{14}\text{C}$  requires around 100 litres, while analysis of the noble gas isotope  $^{39}\text{Ar}$  requires degassing of at least 10 000 litres.

Table 6.1: Summary of groundwater preservation techniques (From US EPA, 1974).

Preservative	Filter	Components Analysed	Container
HCl, pH $\leq 2$	yes	Ca, Mg, Na, K, Fe Mn, Ni, Zn, NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	glass or polythene
H <sub>2</sub> SO <sub>4</sub> , pH $\leq 2$ , 4°C	yes	TOC, NH <sub>4</sub> <sup>+</sup> , Cl <sup>-</sup> , total PO <sub>4</sub> <sup>3-</sup>	glass
NaOH, pH $\geq 12$ , 4°C	no	total CN <sup>-</sup>	glass or polythene
ZnOAc, c. 1 g/dm <sup>3</sup> , 4°C	no	total S <sup>2-</sup>	glass
no additives, 4°C	yes	SiO <sub>2</sub> , Al	plastic

Table 6.2: Summary of the effects of preservatives (From Hitchman, 1983).

Preservative	Effects
Acid (HCl, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> )	Bacterial inhibitor. Metal solvent, preventing precipitation and adsorption to bottle surfaces. Forms salts with organic bases, thus stabilising them.
NaOH	Forms salts and stabilises organic components.
CuSO <sub>4</sub>	Bacterial inhibitor.
ZnOAc	Precipitates sulphide.
Refrigeration at 4°C	Bacterial inhibitor. Slows chemical and physical reactions.

## 7 Solid Samples

There is little point defining a detailed programme of groundwater sampling and analysis without an accompanying programme of rock sampling and characterisation. It is crucially important to correlate groundwater and rock samples to be able to construct realistic models of groundwater evolution. Groundwater compositions reflect the cumulative effects of rock-water interactions over geological time. Chemical equilibria deemed to control the composition of a groundwater should be represented in the rock and fracture filling history of a site. Geochemical modellers should therefore look closely for evidence in the rock/mineral record for rock-water reactions they are hypothesising to occur at a site.

Rock samples will be required from surface outcrops and from the borehole cores (or rock fragments if the boreholes were percussion drilled). In fractured rocks, samples of both the rock mass and the fracture coatings/fills will also be required. In addition, in some instances, it may be useful to collect and analyse samples of the overburden (soils and sediments) since these can affect significantly the composition of the infiltrating groundwater and, thus, the rock-water interaction processes in the shallow rock mass.

### 7.1 Surface samples

It is logical to collect surface rock samples at the time the geological maps of the site and surrounding area are being prepared. Samples should be collected with a sufficiently high density to ensure that lateral variations in rock type, mineralogy and composition are accounted for. As with all geological collecting, effort should be made to collect the freshest possible samples, avoiding strongly weathered, fractured or otherwise altered specimens.

Samples of the overburden, if required, should be collected over the same spatial area as the surface rock specimens. In addition, samples may be required from different depths or as a continuous core through the overburden. Organic rich soils and sediments will need careful preservation to avoid oxic degradation. Once such method is to seal the cores in a wax cover which has the added advantage of stopping desiccation of the sample.

### 7.2 Core samples

The core will probably represent the only available source of rock from depth. Core recovered at the drilling rig will be logged, possibly photographed, cut into sections and stored in core boxes. For crystalline rocks, no special storage

requirements are generally necessary since these types of rock are unlikely to be significantly affected by surface storage. However, for argillaceous rocks, some more specific storage requirements may be necessary, especially if it is planned to extract and analyse the pore fluids contained in the rock specimen.

It is generally not possible nor worthwhile to analyse all of the core and, consequently, representative samples will be selected for examination. It is standard procedure to take for examination slices of the core at regular intervals: the spacing between samples controlled by the heterogeneity of the rock itself. The location (depth) of each slice must be carefully recorded. The remainder of the core is stored for subsequent use as required.

Cores recovered from fractured rocks require that the fracture coatings/infills are sampled in addition to the rock mass. Two types of fracture broadly can be distinguished: closed, hydraulically inactive fractures that represent ancient flow systems; and open, hydraulically active fractures that carry the present-day groundwaters. To understand present-day hydrogeochemical systems fully, it is necessary to ensure that paired rock-water samples are examined. Therefore, every effort should be taken to sample fracture coatings from the same water conducting fractures from which groundwater samples were collected. In this way, the hydrochemistry can be related directly to the mineralogy and geochemistry of the coexisting solid phases: this is especially important for isotopic investigations such as uranium series disequilibrium measurements.

When dividing core samples for analysis, it is worthwhile retaining some sections of each sample for repeat analysis or unforeseen additional tests to supplement the investigations originally planned for.

### 7.3 Analysis

The information to be gained from solid samples is more complex than that from groundwater samples in that, in addition to bulk elemental and isotopic measurements of the whole rock, chemical analyses of individual mineral species and information on the mineralogy and petrology of the rock are also required. As a consequence a whole range of analytical techniques may need to be adopted but all of these are standard geological tools and the necessary expertise will be available in most geological laboratories.

As with the groundwater samples, the rock samples may be analysed at various levels of detail. The routine investigation procedure is likely to include the following aspects:

- ▲ optical microscope investigations of the rock fabric and identification of the mineral

types, and

- ▲ bulk rock major and trace element analyses using X-ray fluorescence (XRF) or inductively coupled mass spectrometry (ICPMS).

In addition to these basic investigations some or all of the following additional studies may be undertaken as required on either rock matrix samples or fracture coatings/fills:

- ▲ detailed mineral identification of mineral separates using X-ray diffraction (XRD) or scanning electron microscopy (SEM),
- ▲ detailed major and trace element chemical analysis of individual minerals using electron or ion-probe, or energy dispersive X-ray (EDAX) coupled to SEM,
- ▲ fluid inclusion chemistry,
- ▲ pore water chemistry,
- ▲ stable isotopic measurements (oxygen and hydrogen) on mineral separates, and
- ▲ uranium-series measurements on mineral separates.

Since these analyses are all standard geological techniques, no details of the analytical procedure or methodologies will be given here.

Throughout the above analysis it is important to recognise sequences of events to be able to identify the most recent processes which may have affected ground-water composition.

## 8 Analytical Programme

Not every water sample will be analysed for all important physico-chemical parameters. It is normal that a restricted suite of analyses are performed on all samples, with a selected set of samples analysed more completely. The more comprehensive analyses are targetted on those samples that are thought to be fully representative of the system; are recovered from an unusual features of the site (*e.g.* a particularly fast-flowing fracture at depth); or display some interesting characteristics on the basis of the restricted analysis programme. There are a number of reasons for limiting the scope of the comprehensive analysis programme but the two most obvious are that certain analysis techniques are very time consuming and expensive, especially some isotopic measurements, and that certain techniques require large amounts of sample and it would be inappropriate and damaging to the system (especially hydrochemically) to collect very large amounts of every sample.

Obtaining high-quality, representative analyses of waters is very difficult since their chemistry may be contaminated or perturbed by many processes during drilling, sampling and storage. To avoid perturbations due to storage and contamination with the atmosphere, certain labile parameters are best measured at the drilling site soon after sampling. Less sensitive parameters can be measured off site at a later time. The SKB site characterisation programme at Aspo adopted the analysis scheme indicated in Table 8.1.

As discussed above, it is normal to have analytical programmes of differing levels of complexity. This is typified by Nagra who, in their groundwater sampling strategy, adopted four analytical programmes (types A to D) of which type D was the most comprehensive. The type A analysis investigated major dissolved species and was used mostly for spring waters and but also for monitoring the quality of groundwaters when boreholes were being flushed as discussed in Section 2.1. Most waters were analysed at the type B and C programmes. The comprehensive, type D programme was used only for selected or particularly interesting water samples. The scope of the type D analysis is illustrated in Figure 8.1.

Often the difference between a 'normal' and a 'comprehensive' analysis scheme is the inclusion of isotopic measurements in the latter. Isotopes are particularly useful because they can tell us information regarding the nature of groundwater that cannot be deduced from the more routine elemental analyses. However, the measurement of isotopes is expensive, time-consuming and often requires large sample volumes and, consequently, is limited to selected samples. In particular, isotopic data can provide information concerning infiltration conditions, groundwater mixing, groundwater evolution, residence times and contamina-



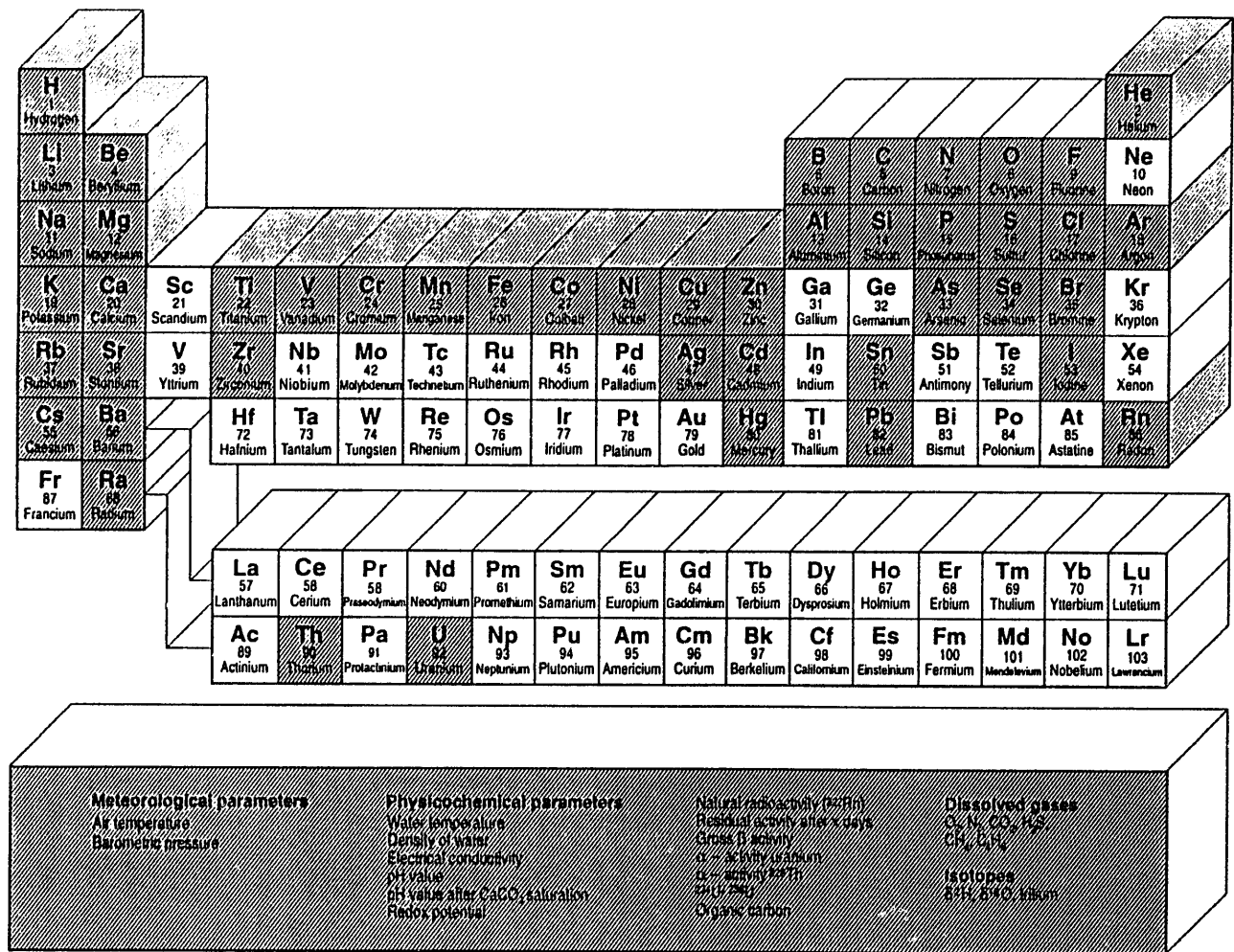


Figure 8.1: Nagra type D analysis programme (From Gautschi and Scholtis, 1989)

Table 8.1: SKB groundwater analysis scheme.

Analysis	Physico-chemical parameter
<i>Downhole probe</i>	pH, Eh, pS, T, P
<i>Surface flow through cell</i>	pH, Eh, pS, pO <sub>2</sub> , EC, T
<i>Field laboratory</i>	
Drilling water content	tracer (Uranine)
Dissolved constituents	Na, K, Ca, Mg, HCO <sub>3</sub> , Cl, SO <sub>4</sub> , SiO <sub>2</sub> , Fe <sup>2+</sup> , Fe <sub>total</sub> , HS <sup>-</sup> , Mn <sup>2+</sup> , F, PO <sub>4</sub> , Br, N-NO <sub>2</sub> , N-NH <sub>4</sub>
<i>Off site laboratory</i>	
Dissolved elements	N-NO <sub>2</sub> , N-NO <sub>3</sub> , Sr, Li, Al, I, U, Ra, Rn, Th, trace elements
Filter residues	Ca, Fe, Si, S
Isotopes	<sup>2</sup> H, <sup>3</sup> H, <sup>13</sup> C, <sup>14</sup> C, <sup>18</sup> O, <sup>234</sup> U, <sup>235</sup> U, <sup>238</sup> U
Organics	TOC
Gases	N <sub>2</sub> , H <sub>2</sub> , O <sub>2</sub> , CH <sub>4</sub> to C <sub>4</sub> H <sub>10</sub> , He, CO <sub>2</sub> , CO, Ar

tion.

## 8.1 Quality issues

In terms of geochemical modelling, there are a number of issues and questions the modeller should ascertain about each groundwater analysis:

- ▲ what errors (sampling and analytical) are associated with each analysis? Quality scores from assessments of sampling procedures are relevant, together with analytical errors and detection limits. These errors should be represented on plotted data using error bars.
- ▲ the balance of anionic and cationic charges should be better than  $\pm 5\%$ . Analyses with charge balances outside this range should be viewed as suspect.
- ▲ total dissolved solids contents determined by evaporation and weighing of residual salts should match those calculated from the summation of analytical concentrations within  $\pm 5\%$ ;

- ▲ analytical detection limits for dissolved aluminium should be as low as possible to be able to determine likely concentrations in groundwater ( $< 0.2$  mg/l).

## 9 Data Recording and Presentation

The geochemical data acquired in a site characterisation programme will be extensive. There will be data from both solid and water samples, with each sample may be having been analysed for between 20 to 30 physico-chemical parameters. It is quite possible, therefore, in a large programme to acquire in the order of  $10^4$  individual measurements. Integration and interpretation of these data is aided if the data are maintained in a flexible database system. However, the output relies on the care (Quality Assurance) with which the data entry was planned and executed. Ideally, the information handling system or systems should provide the following:

- ▲ facilities for the storage of information produced in the geochemistry investigations together with information from other studies such as geology, geophysics, hydrogeology *etc*;
- ▲ retrieval and manipulation of the information so that any data set can be quickly recalled, modified and compared with other datasets using statistical correlation methods; and
- ▲ display of the results in formats which allow the results to be readily understood by the user.

The last point is particularly important. By the nature of geological and geochemical data, it is best displayed as either a two-dimensional cross-section through the site or, better still, as a three-dimensional model. Computer packages (*e.g.* EarthVision) have recently become available that can combine three-dimensional visualisation capabilities with data interpretation (statistical) packages that allow the user to display data from different sources; *e.g.* can overlay hydrochemical data on top of fault and fracture patterns in a three-dimensional mode. Such packages make the integration and interpretation of data, and correlation between different data sets, much more practical than previous manual techniques.

## **10 Conclusions**

The geochemical modeller must be aware of all potential uncertainties in groundwater compositional data used to establish models of groundwater or repository evolution. Uncertainties arise from: sampling; filtration and preservation; corrections for drill fluid contamination; sample depressurisation; and chemical analysis. These uncertainties must be adequately represented in data interpretation.

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