P-04-109

Forsmark site investigation

Hydrochemical characterisation in KFM04A

Results from two investigated borehole sections, 230.5-237.6 and 354.0-361.1 metres

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June 2004

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Abstract

Complete chemical characterisation has been conducted in two sections, 230.5-237.6 and 354.0-361.1 m, of borehole KFM04A. Complete chemical characterisation is the most extensive chemical investigation method performed in core drilled boreholes. The method entails pumping, measurements on-line and regular water sampling for chemical analyses in isolated borehole sections during approximately three weeks per section.

The results obtained from the investigation includes on-line measurements of redox potential, pH, dissolved oxygen, electric conductivity and water temperature in the borehole section as well as chemical analyses of major constituents, trace components and isotopes. Gas content and composition, inorganic colloids as well as humic and fulvic acids in the groundwater were not investigated due to high flushing water content and poor redox measurements.

The water composition was stable during the entire pumping and sampling periods and the chloride concentration amounted to approx. 5600 mg/L in both sections. No reliable redox potential data were obtained, but iron was present as ferrous iron at an unusually high concentration. Severe corrosion was discovered on the downhole equipment after each measurement period in the borehole.

Sammanfattning

Fullständig kemikarakterisering har utförts i två sektioner av borrhålet KFM04A, nämligen vid 230.5-237.6 och 354.0-361.1 m. Fullständig kemikarakterisering är den mest omfattande undersökningsmetoden som utförs i kärnborrhål. Metoden innebär pumpning, mätningar on-line och regelbunden vattenprovtagning för kemiska analyser i avmanschetterade borrhålssektioner under cirka tre veckor per sektion.

De resultat som erhållits från undersökningen omfattar on-line mätningar av redox-potential, pH, syre, elektrisk konduktivitet och temperatur samt kemiska analyser av huvudkomponenter, spårämnen och isotoper. Gasinnehåll och gassammansättning, oorganiska kolloider samt humus och fulvosyror undersöktes inte på grund av hög spolvattenhalt och icke trovärdiga redoxmätningar.

Vattensammansättningen var stabil under pump- och provtagningsperioderna och kloridhalten uppgick till cirka 5600 mg/L i båda sektionerna. Inga trovärdiga redox data erhölls, men järn förekom som tvåvärt järn i ovanligt hög koncentration. Allvarliga korrosionsskador upptäcktes på borrhålsutrustningen efter varje mätperiod i borrhålet.

Contents

1 Introduction

This document reports the performance and results from the activity: ”Complete chemical characterisation” in the cored borehole KFM04A within the site investigation at Forsmark /1/. The work was conducted according to the activity plan AP PF 400-04-01 (SKB internal controlling document). The report presents hydrochemical data from the following two borehole sections:

- 230.5-237.6 m (Complete chemical characterisation, conducted by ÅF Energi och Miljö AB)
- 354.0-361.1 m (Complete chemical characterisation, conducted by ÅF Energi och Miljö AB)

The fieldwork was carried out during the period January 2004 – April 2004.

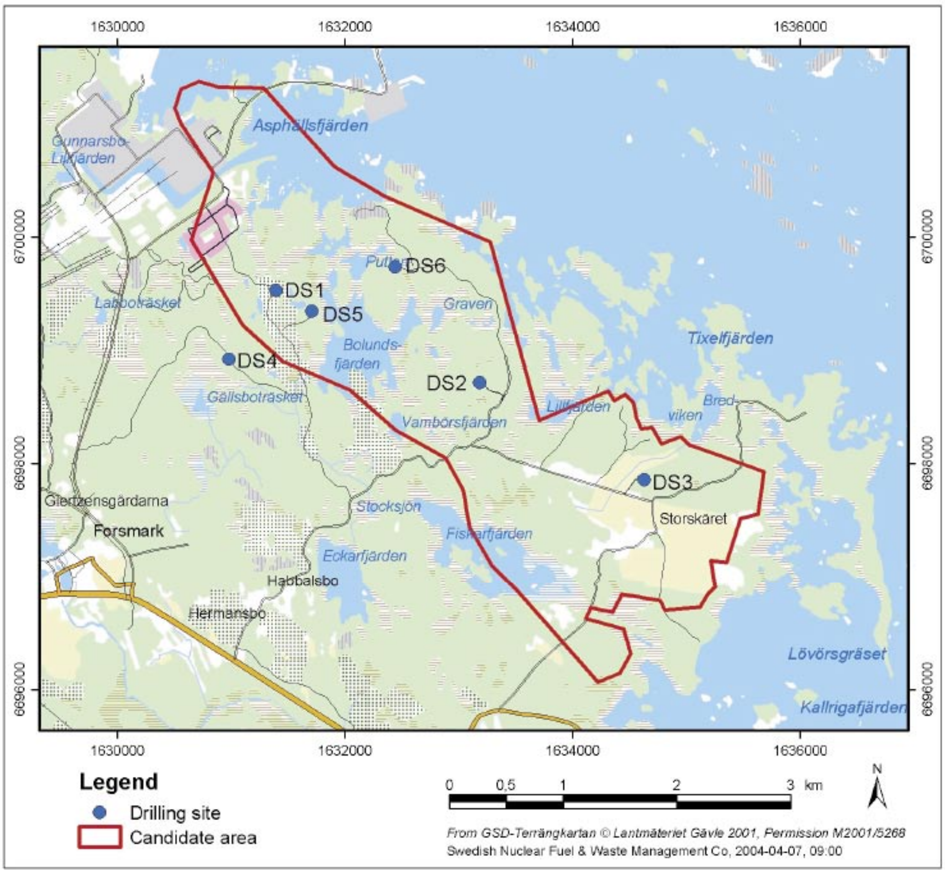
Borehole KFM04A is the fourth telescopic borehole drilled at Forsmark /2/. It has an inclination of 60 degrees from the horizontal plane and penetrates the altered zone at the border of the candidate area. The location of the current drilling sites within the investigation area are shown in Figure 1-1, whereas Figure 1-2 is a detailed map of drilling site DS4 with the borehole KFM04A and adjacent percussion boreholes and shallow monitoring wells. The borehole section between 0-100 m is percussion drilled and the first 100 m are cased with a stainless steel casing with the internal diameter of 200 mm, whereas the 100-1002.4 m interval is core drilled with a diameter of 77 mm. The technical design of the borehole is presented in Appendix 1.

The borehole is of the so called SKB chemical-type, see method descriptions MD 620.003 (Method description for drilling cored boreholes) and MD 610.003 (Method description for percussion drilling). A SKB chemical-type borehole requires cleaning procedures to be carried out on all downhole equipment both during and after drilling, according to level 2 in the cleaning instructions outlined in MD 600.004 (Instruktion för rengöring av borrhålsutrustning och viss markbaserad utrustning). All method descriptions and instructions are SKB internal controlling documents.

The data references to the present activity are given in Table 1-1.

Table 1-1. Data references.

Activity	Database	Identity number
Hydrochemical characterisation in KFM04A	SICADA	Field Note No.
230.5-237.6 m		Forsmark 261
354.0-361.1 m		Forsmark 306



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Swedish Nuclear Fuel & Waste Management Co, 2004-04-07, 09:00

Figure 1-1. *The investigation area at Forsmark (approximately the area inside the black square) including the candidate area selected for more detailed investigations. The six drilling sites for deep boreholes, DS1-6, are marked with blue circles. Borehole KFM04A is situated at drilling site DS4.*

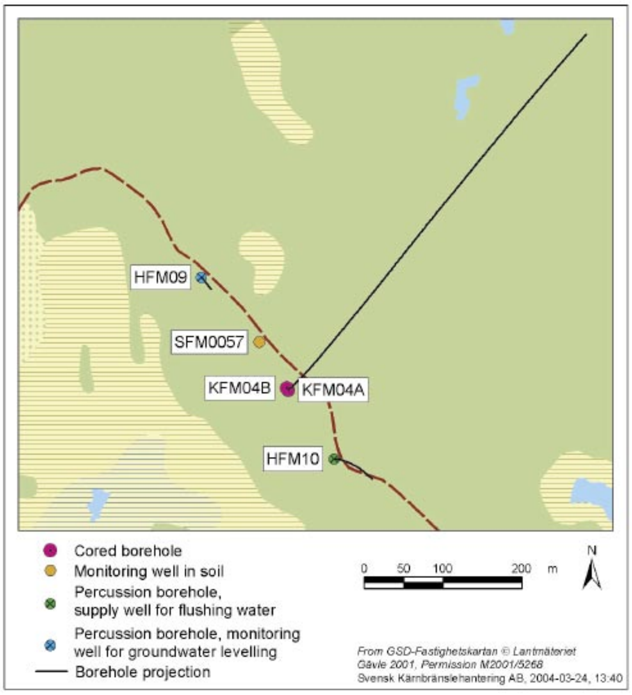

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Figure 1-2. *Location of the cored borehole KFM04A, the percussion boreholes and the monitoring wells at drilling site DS4.*

2 Objective and scope

“Complete chemical characterisation” is the most extensive chemical investigation method performed in core drilled boreholes. The method is carried out in order to obtain as much information as possible about the groundwater chemical conditions in individual water bearing fractures or local minor fracture zones. Considerable effort is put on obtaining representative samples from a limited rock volume. Careful pumping and continuous control of the pressure in the sampled borehole section, as well as above the section, is maintained in order to minimize the risk of mixing with water from other fracture systems.

The borehole KFM04A has an inclination of 60 degrees and intersects the altered zone that constitutes the border of the tectonical lens/candidate area. During the drilling it became evident that all or most of the flow yielding fractures were located in the part of the borehole that intersects the altered zone. The deep groundwater from all of the previously investigated core drilled boreholes KFM01A, KFM02A and KFM03A was collected in another type of bedrock in the central part of the tectonic lens. Therefore, the groundwater from the water bearing sections in KFM04A was particularly interesting to investigate, as it represents a somewhat different geological environment.

The analysis programme was carried out according to the SKB Class 4 and Class 5 levels, including all options. In addition, pH, redox potential (Eh) and water temperature were measured in a downhole flow-through cell as well as at the surface. Surface measurements also included electric conductivity and dissolved oxygen.

The investigation method normally includes collection of in situ samples to determine a) gas content and composition, b) microbe content and characterisation, and c) colloid content and composition. However, these analyses were cancelled as were fractionation of organic acids and inorganic species as well as enrichment of organic acids for determination of determine $\partial^{13}C$ and pmC (percent modern carbon). The reason for this was high content of flushing water and poor redox measurements.

3 Background

3.1 Flushing water history

The percussion drilled borehole HFM10 served as supply well for the flushing water used for drilling of the borehole KFM04A /3/. The chemical composition of the flushing water was checked before and during use. The analytical data from the supply well HFM10 are reported in /4/. The core drilling of the 1002 m long borehole consumed approximately 1000 m^3 of flushing water (a faulty flowmeter recorded 655 m^3) and the volume of returned water pumped from the borehole during drilling was 3470 m^3. The nominal concentration of the dye Uranine, added as a tracer to mark the flushing water, was 0.2 mg/L. The Uranine concentration in the flushing water was checked regularly during the drilling and a total of 74 samples were analysed. The average Uranine concentration in the sample series was 0.089 ± 0.093 mg/L. The Uranine concentrations in the sample series of flushing water as well as return water are presented in Figure 3-1. Further, the amount of Uranine added to the borehole via the flushing water and the estimated amount recovered in the return water is given in Table 3-1.

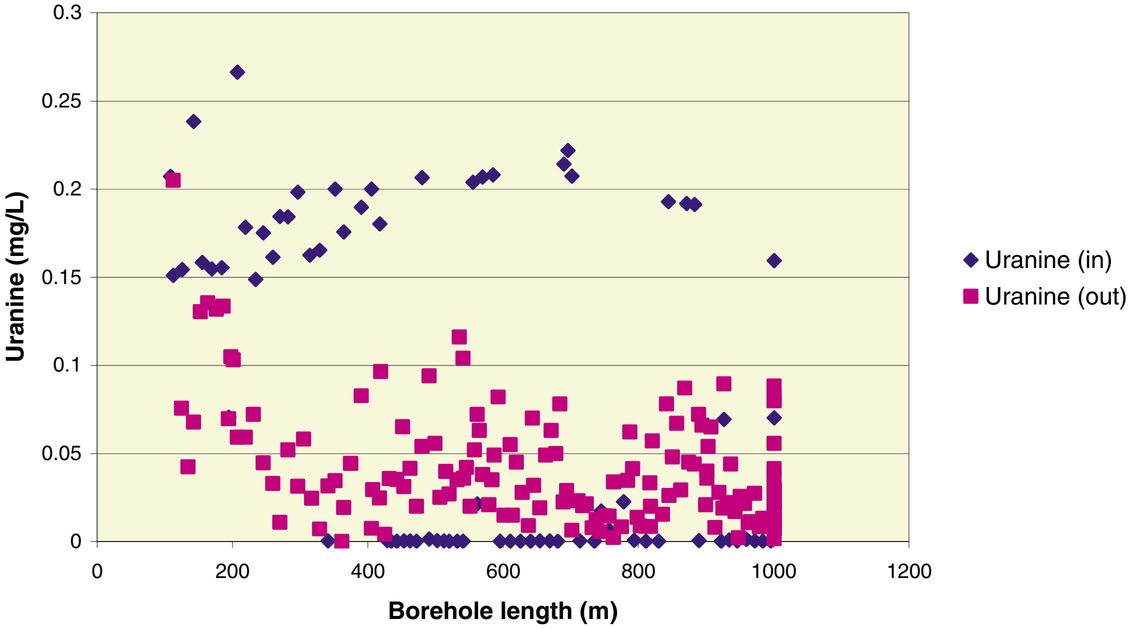


Figure 3-1. *Uranine concentrations in the flushing water and in the return water versus borehole length. The addition of Uranine was done using automatic dosing equipment controlled by a flow meter. Malfunction of the flow meter caused irregular and erroneous dosing of Uranine and the estimation/calculation of the flushing water content in the subsequently collected water samples are unreliable.*

Table 3-1. Amount of Uranine added in KFM04A via the flushing water during core drilling and the amount recovered from the mammoth pumping.

	Uranine (g)
Amount of Uranine added to the borehole via the flushing water according to log book.	165
Amount of Uranine added to the borehole via the flushing water as calculated from average Uranine concentration and total volume of flushing water.	88
Amount of Uranine recovered in the return water as estimated from average Uranine concentration and total volume of return water.	145

The Uranine budget in Table 3-1 suggests that at least 100 m^3 of the flushing water was lost to the borehole and the adjacent host bedrock. The disagreement between the calculated amount of Uranine and the added amount according to the log book demonstrates the large uncertainty in the estimations using average Uranine concentrations. However, in this borehole the sampling frequency of return water was increased compared to when drilling the previous telescopic boreholes and the calculation of recovered Uranine is based on 151 samples compared to the 74 samples of flushing water.

As the borehole KFM04A is of SKB chemical-type, the following special precautions were taken in order to minimize contamination via the flushing water:

- The supply well was also of SKB chemical-type.
- The concentration of total organic carbon (TOC) should preferably be below 5 mg/L to avoid effects on the microbiological conditions in the borehole. The borehole HFM10 was selected as flushing water supply well and the concentration of total organic carbon (TOC) was in the range 2.3-2.9 mg/L.
- The dosing equipment for Uranine that was introduced during the drilling of KFM02A was used also in KFM04A. This made it possible to remove the storage tank for flushing water after the UV-system.

Analyses of the microbe content in the flushing water, before and after the UV-system, was performed during drilling /5/. The results showed that the amount of algae and bacteria in the flushing water entering the borehole was smaller compared to the situation in KFM01A, probably due to the absence of the in-line storage tank after the UV-system. However, the microbe content was still too high to be satisfactory and further measures need to be taken in order to avoid microbial growth in the flushing water in future drilling activities.

3.2 Previous events and activities in the borehole

KFM04A is a SKB chemical-type core borehole and thus specially intended for complete hydrochemical characterisation. Only investigations that are necessary in order to select suitable borehole sections are carried out in the borehole prior to the chemistry campaign. The more equipment that is used in the borehole, the greater is the risk of contamination and effects on the in situ microbiological conditions. The activities/investigations performed in KFM04A prior to the chemistry campaign are listed in Table 3-2 below.

Table 3-2. Activities performed in borehole KFM04A prior to the hydro-chemical characterisation.

Activities performed	Date of completion	Length or section (m)	Comment
Percussion drilling	2003-05-27	0 – 107.42	-
BIPS logging	2003-06-02	11 – 106.5	-
Geophysical logging (radar)	2003-06-03	10-100	-
Casing installed	2003-06-26	0 – 106.91	No initial hydraulic test was performed in the percussion drilled part of the borehole (0-107.42 m).
Core drilling	2003-10-30	107.42-1001.42	HFM10 was the source of flushing water for drilling the cored part of KFM04A. HFM10 is a SKB chemistry type of borehole /2, 3, 4/.
Water sampling, Wireline sond	2003-09-11	226-418	WL-sond water sampling failed at two occasions due to clogging problems, drilling debris in the inclined boreholet, no samples.
Flushing water treatment	-	-	The automatic dosing of Uranine that was introduced in KFM02A, was used also during the drilling of KFM04A. In this way no storage tank was needed after the UV-system /2/.
Check of microbe content in flushing water	2003-10-14	-	/5/
Geophysical logging	2003-12-07	0-1000	Several logging methods.
BIPS-logging	2003-12-08	108-1000	–
Hydrochemical logging	2003-12-08	0-995	High flushing water content along the borehole (about 30-40 % beteeen 200-600 m and cirka 50 % below 600 m depth) /6/.
Hydrochemical characterisation	2004-05-11	-	Presented in this report.

3.3 Choice of borehole sections

The first investigated borehole section in borehole KFM04A was selected without information from difference flow logging. The borehole was available for chemical investigations from the beginning of January 2004, but the difference flow logging activity was planned to be conducted as late as in May. However, already during drilling, it was evident that all or most of the flow yielding fractures were located in the part of the borehole that intersects the altered zone. It was found that a very dominating water bearing fracture zone was located at about 232 m borehole length. In order to gain time and have the possibility to include chemical data from this borehole in data freeze 1.2, it was decided to investigate a section at 230.5 – 237.6 m.

A break in the investigation for service and modification of the downhole equipment as well as changed planning at the site investigation in Oskarshamn made it possible to conduct difference flow logging /7/ of the borehole already in March 2004.

Due to available new flow information and the chance of having lower flushing water content in a less conductive borehole section, the investigation was continued in a new section, 354.0-361.1 m, after the service break.

Table 3-3. Selected sections, fractures/fracture zones and hydraulic transmissivity in borehole KFM04A.

Section (m)	Dominating water bearing fractures (m)	T (m^2/s)
230.5-237.6	232.7 235.6	4.6E-5*
354.0-361.1	359.8	1.3E-6*

* Value from preliminary evaluation for entire section.

4 Equipment

4.1 The mobile field laboratory

The mobile field laboratories used by SKB for water sampling and downhole measurements consist of a laboratory unit, a hose unit with downhole equipment and a Chemmac measurement system in a separate wagon unit (MYC); the equipment is presented schematically in Figure 4-1. The different parts of the system are described in the SKB internal controlling documents SKB MD 434.004, 434.005, 434.006, 434.007 and SKB MD 433.018 (Mätsystembeskrivningar för mobil kemienhet allmän del, slangvagn, borrhålsutrustning, mobil ytChemmac och dataapplikation).

The Chemmac measurement facilities include communication systems, measurement application and flow-through cells with electrodes and sensors at the ground surface (surface Chemmac) and in the borehole (borehole Chemmac).

The downhole equipment consists of inflatable packers, pump, borehole Chemmac and the in-situ sampling unit (PVP) allowing measurement (borehole Chemmac) and sampling in-situ in the borehole section (PVP sampling unit). The four sample portions collected with the PVP sampling unit maintain the pressure from the borehole section when lifted to the surface. The portions are used for colloid filtration, gas analyses and microbe investigations.

The mobile units used in borehole KFM04A, section 230.5-237.6 m and 354.0-361.1 m consisted of the hose unit S2, the laboratory unit L3 and the MYC 2 unit for Chemmac measurements and computer work.

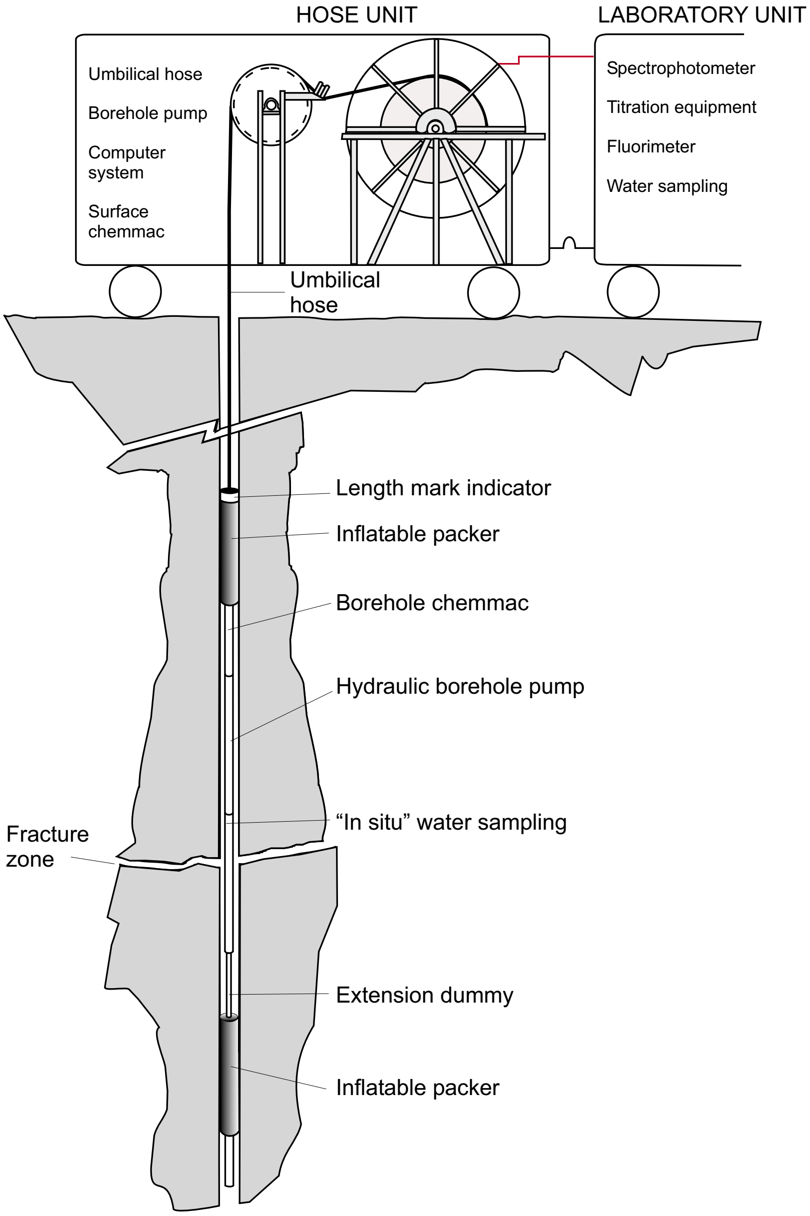


Figure 4-1. *A schematic presentation of a mobile field laboratory; hose unit, laboratory unit and downhole equipment. The configuration of the downhole units in the borehole can be varied depending on desired section length. However, the in-situ water sampler must always be positioned first in the sample water path.*

5 Performance

Complete chemical characterisation of the two sections in borehole KFM04A was performed according to activity plan AP PF 400-04-01 (SKB internal controlling document) following the method described in SKB MD 430.017 (Metodbeskrivning för fullständig kemikarakterisering med mobilt fältlaboratorium, SKB internal controlling document).

The investigation sequence is given in Table 5-1.

Table 5-1. Investigation sequence in KFM04A.

Event	Borehole section (m)	Start date	Stop date	Comment
Interrupted test Complete chemical characterisation.	230.5-237.6	2004-01-09	2004-02-17	Pumped volume: 8.4 m^3. Final flushing water content: 7.6-15.1 % (uncertain value).
BIPS-logging.	-	2004-03-08	2004-03-09	Repeated logging, drilling debris caused bad quality the first time.
Difference flow logging.	100-1000	2004-03-10	2004-03-27	/7/
Complete chemical characterisation.	354.0-361.1	2004-04-14	2004-05-11	Pumped volume: 6.0 m^3. Final flushing water content: 6.5-15 % (uncertain value).

5.1 Overview of field work procedure

A short chronological summary of the different steps that constitute chemical characterisation of groundwater in a borehole section is given below.

The preparations that are conducted before the downhole equipment is lowered in the borehole include:

- Cleaning of the inside of the sample water channel in the umbilical hose. (Before the first lowering to section 230.5-237.6 m, the umbilical hose was cleaned with 0.5 M nitric acid, followed by rinsing to neutral pH with de-ionised, deoxygenated water. Before the next lowering and before the lowering to section 354.0-361.1 m, only de-ionised water was used for cleaning.) Finally, the sample water channel is filled with de-ionised and deoxygenised water prior to the lowering.
- Cleaning and preparation of the four sample containers (PVB) belonging to the in- situ water sampling unit (PVP). The containers are cleaned using 70 % denatured ethanol. One of the containers is used for microbe sampling and sterile conditions are desirable. The containers are purged with nitrogen gas and a small nitrogen gas pressure is maintained in the containers. The magnitude of the pressure depends on the depth of the section to be sampled.
- Calibration of the pH and redox electrodes in the borehole Chemmac.

The different downhole units are assembled during lowering of the equipment in the borehole and the following steps are taken:

- The outside of the umbilical hose/pipe string is cleaned with 70 % denatured ethanol (SKB MD 600.004).
- Calibration of the umbilical hose length is conducted at least once in each investigated borehole. For this, a length mark detector unit (caliper) is mounted together with the standard downhole equipment. The length mark detector indicates length calibration marks milled into the borehole wall with (normally) 50 m distance /2/. At each indication, a reading is made of the corresponding length mark on the umbilical hose. The correct distance to each length mark is obtained from the SICADA database.

When the pump is started and the packers are inflated at the desired positions in the borehole, a pumping and measurement period begins. Typical measures taken and activities carried out during this period are:

- Calibration of the pH and redox electrodes as well as the electric conductivity and oxygen sensors in the surface Chemmac is conducted when the pumped water from the borehole section has reached the surface.
- Careful attention is paid in order to ensure that the packed off section is well isolated from the rest of the borehole. A significant drawdown in the section during pumping is one indication that the section is isolated. Leakage would cause pumping of water from the borehole column above and/or below the packers and not only from the fracture zone of interest. However, the drawdown in the borehole section must not be too large since the greater the drawdown, the larger the bedrock volume affected by the pumping and the risk of mixing with water from other fracture systems increases. The pumping flow rate is adjusted (between 50 and 300 mL/min) depending on the flow yield from the fracture or fracture zone and maintained more or less constant during the pumping and measurement period.
- Water samples are collected regularly twice a week during the pumping period. Changes in water composition are monitored by conductivity measurements and by immediate analyses at the site.
- A decision when to terminate the sampling work in the section is made at the end of the third week of the pumping and measurement period. The investigation might be prolonged if the concentration of flushing water exceeds 1 % or if the redox potential measurements have not reached stable values. A final SKB Class 5 sample including all options is collected the day before termination.

Completion of the investigation in the section and lifting of the downhole equipment entails:

- Following stopping of the borehole pump and deflation of the packers, the equipment is lifted and the different downhole units are de-assembled.
- Calibration of the electrodes in the borehole Chemmac and surface Chemmac. The final calibration for a section can be used as the initial calibration for the next section.

5.2 Performance in section 230.5-237.6 m

The configuration of the downhole equipment in the borehole was, from the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP) and lower packer, see Appendix 3, Figure A3-2. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping was performed at an irregular flow rate varying from about 100 mL/min to 260 mL/min. A diagram showing the pressures within and above the borehole section as well as the flow rate during the pumping/measurement period is presented in Appendix 4, Figure A4-1.

The events during the investigation are listed in Table 5-2.

Table 5-2. Events during the pumping/measurement period in section 230.5-237.6 m.

Date	Events *Improvement/deviation**	SKB sample no.
040108	Calibration of borehole Chemmac.	
040109	Lowering of downhole equipment (230.50-237.64). Start of borehole pump.	
040112	Problem with surface Chemmac calibration, electric noice.	
040116	Calibration of surface Chemmac.	
040116	Water sampling: SKB class 4.	8154
040120	Water sampling: SKB class 4.	8155
040122	Water sampling: SKB class 5.	8156
040123	Humic and fulvic acids; enrichment start.	
040127	No water flow, pump failure (interruption 040125 23:30 according to logged values).	
	Humic and fulvic acids; enrichment interrupted.	
	Lifting.	
040130	Broken spring in borehole pump.	
	Severe corrosion discovered on downhole units. Change to spare units.	
040202	Calibration of borehole Chemmac.	
	Lowering of downhole equipment (230.50-237.64).	
040204	Water sampling: SKB class 2.	8157
040205	Water sampling: SKB class 4.	8160
040210	Water sampling: SKB class 5.	8267
040212	Water sampling: SKB class 4.	8269
040217	No water flow, pump failure. Lifting. Calibration of borehole Chemmac was not performed.	
	Broken spring in borehole pump.	
	Severe corrosion discovered also on these downhole units.	
	It was decided to take care of the damages caused by corrosion and to modify the equipment (change of umbilical hose) before continuing the measurements in the borehole.	

*nonconformity report

5.3 Performance in section 354.0-361.1 m

The configuration of the downhole equipment in the borehole was, from the top: umbilical hose, length mark detector, borehole Chemmac, upper packer, borehole pump, in situ water sampler (PVP) and lower packer, see Appendix 3, Figure A3-6. The pressures above and within the section were measured by the borehole Chemmac unit and the PVP water sampling unit, respectively.

The pumping was performed at a flow rate of about 160 mL/min. A diagram showing the pressures within and above the borehole section as well as the flow rate during the pumping/measurement period is presented in Appendix 4, Figure A4-2.

The events during the investigation are listed in Table 5-3.

Table 5-3. Events during the pumping/measurement period in section 354.0-361.1 m.

Date	**Events** _**Improvement/deviation***_	**SKB sample no.**
040414	Lowering of downhole equipment (354.00-361.13 m).	
	Calibration of borehole Chemmac.	
040419	Calibration of surface Chemmac.	
040506	No electric power due to earth fault breaker.	
040420	Water sampling: SKB class 4.	8283
040428	Water sampling: SKB class 4.	8285
040504	Water sampling: SKB class 5.	8286
040510	Water sampling: SKB class 5 (all options).	8287
040511	Lifting	
040511	*Severe corrosion discovered on the downhole equipment.*	
	Calibration of borehole Chemmac.	
	Calibration of surface Chemmac.	
	The calibration data from surface Chemmac pH 4 are missing due to overwriting of calibration file. Lack of calibration solution is the reason why no recalibration was made.	
040512	Sampling of sterile water in PVB-unit for check of cleaning, “microbe blank”.	
040512	*Packer leakage when the water sample for “microbe blank” was collected.*	

* nonconformity report

5.4 Water sampling, sample treatment and analyses

The pumped water from the borehole section is led into the laboratory unit (section 230.5-237.6 m) or the MYC-unit (section 354.0-361.1 m) if the laboratory unit is not available. In either case, filtration of sample portions is performed on-line by connecting the filter holders directly to the water outlet. A water sample is defined as water collected during one day and consists of several sample portions, labelled with the same sample number.

An overview of sample treatment and analysis methods is given in Appendix 7. The routines are applicable independently of sampling method or type of sampling object.

6 Nonconformities

The hydrochemical characterisation of the two investigated sections in KFM04A has been conducted according to the SKB internal controlling documents AP PF 400-04-01, SKB MD 430.017 and 430.018. Severe corrosion on the downhole equipment occurred during each measurement period in the borehole and was caused by electrochemical phenomena, possibly due to ground currents, in the part of the borehole that intersects the altered zone. An investigation concerning the corrosion problem has been initiated after completion of the chemical investigation. Besides the corrosion, the following deviations from programme and disturbances should be mentioned.

- Equipment malfunctions during the pumping/measurement periods, listed in Tables 5-2 and 5-3.
- The redox measurements were not successful in either borehole section. The reason is probably the corrosion reactions mentioned. Also, the pH electrodes in borehole Chemmac gave unstable and non-consistent responses.
- Electric conductivity and dissolved oxygen measurement data from the first part of the measurement sequence in section 230.5-237.6 m were omitted, since the water flow was affected by ice formation inside the inlet to the surface Chemmac.
- The calculation/estimation of the flushing water content in each sample is rather uncertain, since the Uranine concentration in the flushing water, added to the borehole during drilling, varied considerably from time to time.
- The allowed upper limit for flushing water content (1 %) was exceeded and amounted to between 7 and 15 % (uncertain values) in both sections. This is not reported in deviation reports. However, studies such as colloid filtration, sampling of gases and microbes as well as fractionation of organic acids and enrichment of organic acids were cancelled because the flushing water content was considered too high.

7 Data handling and interpretation

7.1 Chemmac measurements

The processing of Chemmac data are described in SKB MD 434.007-02 (Mätsystembeskrivning för Chemmac mätsystem, SKB internal controlling document, in progress).

7.1.1 Data file types and calculation software

The on-line measurements in a borehole section produces the following types of raw data files:

- Calibration files from calibration measurements (*.CRB) and corresponding comment files (*.CI). The files are used for calculation of calibration constants (pH and Eh) and the calibration factor (electric conductivity). For surface Chemmac ten *.CRB and ten *.CI files are produced and for borehole Chemmac six *.CRB and six *.CI files.
- Raw data file containing the logged measurements from the borehole section and the surface (*K.MRB) as well as a corresponding comment file (*.MI). The logged voltage values need to be converted to pH and Eh values (also in mV) using the calibration constants obtained from calibration.
- Measurement file including equipment and environment parameters (*O.MRB), such as power consumption in the downhole Chemmac unit and temperature inside the hose unit.

The original raw data files as listed above are stored in the SICADA file archive. The raw data are re-calculated and evaluated in order to obtain pH and redox potential values and to correct the electric conductivity values using the specially designed calculation software (Hilda). The resulting files containing calculated and evaluated values as well as comments on the performance are:

- A file *constants.mio containing all the calculated calibration constants (one constant for each electrode in each buffer solution). The file is stored in the SICADA file archive and is useful in order to follow the development of single electrodes.
- A file *measurements.mio containing the calculated and evaluated measurement values (pH, redox potential, electric conductivity and water temperature). The data from the file are exported to the data tables "redox" and "ph_cond" in SICADA. As the file also contains some measured parameters that are not included in the tables mentioned above (e.g. pressure registrations), the complete file is also stored in the SICADA file archive.
- A file *comments.mio containing comments on the fieldwork and the calculation/evaluation. The comments in the file are imported as activity comments to SICADA.

7.1.2 Calculations and evaluation of pH and redox potential

The redox potential is measured by three electrodes at the ground surface and three in the borehole section. Further, pH is measured by two electrodes at the ground surface and two in the borehole section. The registrations made by the redox and the pH electrodes are logged each hour during a measurement period of approximately three weeks and a calibration is performed before and after each measurement period. The treatment of the raw data includes the following steps:

- Calculation and choice of calibration constants.
- Calculation of one pH and one redox potential sequence for each electrode (i.e. three or six redox electrodes and two or four pH electrodes).
- Determination of representative pH and redox potential values as well as estimated measurement uncertainties for the investigated borehole section.

One calibration constant is selected for each electrode using one of the following alternatives:

- Case 1: Calculation of the average calibration constant value and the standard deviation. The initial and the final calibration measurements result in four constants for each redox electrode (in pH 4 and pH 7 buffer solutions) and six constants for each pH electrode (in pH 4, 7 and 10 buffer solutions).
- Case 2: The calibration constant obtained from the initial calibration measurement at pH 7 is selected because it is closest to the pH of the borehole water. This alternative is chosen if the calibration constants obtained in the different buffers show a large variation in value (generally a difference larger than 20 mV between the highest and the lowest value). The standard deviation is calculated in the same way as in Case 1.
- Case 3: If the final calibration constants turn out to be very different (more than 20 mV) from the initial constants, a linear drift correction is needed. The reason is most often a drift in the reference electrode. The average values and standard deviations are calculated for the initial and the final calibration constants separately and a linear correction is made between the selected initial and the selected final constant. The higher of the two standard deviation values is used in the estimation of the total measurement uncertainty.

The values in the measurement raw data file are converted to pH and Eh measurement sequences for each pH and redox electrode using the calibration constant selected as stated above.

The next step is to choose a logging occasion in a stable part of the measurement period and select a result for each electrode. The average values are calculated for each electrode group in order to obtain one representative value of redox potential, pH (borehole Chemmac) and pH (surface Chemmac), respectively. Obviously erroneous electrodes are omitted. The corresponding total measurement uncertainties are estimated using the standard deviations of the calibration constants and the standard deviations of the Eh and the pH values obtained by the different sets of electrodes. It is useful to evaluate pH at the surface and pH in the borehole section separately, since pH in the pumped water might differ from the pH measured in the borehole section. This is due to changing gas pressure conditions and its effects on the carbonate system.

Factors considered when evaluating the measurement uncertainties in pH and redox potential (Eh) values are:

- Difference in calibration constants for each electrode and calibration/buffer solution.
- Drift in calibration constants between the initial and the final calibration.
- Stability in voltage value during the last part of the on-line measurement. A successful measurement shows no drift tendencies.

- Agreement between the different pH and redox electrodes on the surface and in the downhole borehole Chemmac.
- Number of electrodes showing reasonable agreement. Obviously erroneous electrodes are excluded from the calculation.

7.2 Water analysis data

The following routines for quality control and data management are generally applied for hydrogeochemical analysis data, independently of sampling method or type of sampling object.

Some of the components are determined by more than one method and/or laboratory. Moreover, duplicate analyses by an independent laboratory are performed as a standard procedure on each fifth or tenth collected sample. All analytical results are stored in the SICADA database. The applied hierarchy path "Hydrochemistry/Hydrochemical investigation/Analyses/Water in the database" contains two types of tables, raw data tables and primary data tables (final data tables).

Data on basic water analyses are inserted into the raw data tables for further evaluation. The evaluation results in a final reduced data set for each sample. These data sets are compiled in a primary data table named "water composition". The evaluation is based on:

- Comparison of the results from different laboratories and/or methods. The analyses are repeated if a large disparity is noted (generally more than 10 %).
- Calculation of charge balance errors. Relative errors within ± 5 % are considered acceptable (in surface waters ± 10 %).

$$\text{Relative error } (\%) = 100 \times \frac{\sum cations(equivalents) - \sum anions(equivalents)}{\sum cations(equivalents) + \sum anions(equivalents)}$$

- General expert judgement of plausibility based on earlier results and experience.

All results from special analyses of trace metals and isotopes are inserted directly into primary data tables. In those cases where the analyses are repeated or performed by more than one laboratory, a "best choice" notation will indicate those results which are considered most reliable.

An overview of the data management is given in Figure 7-1.

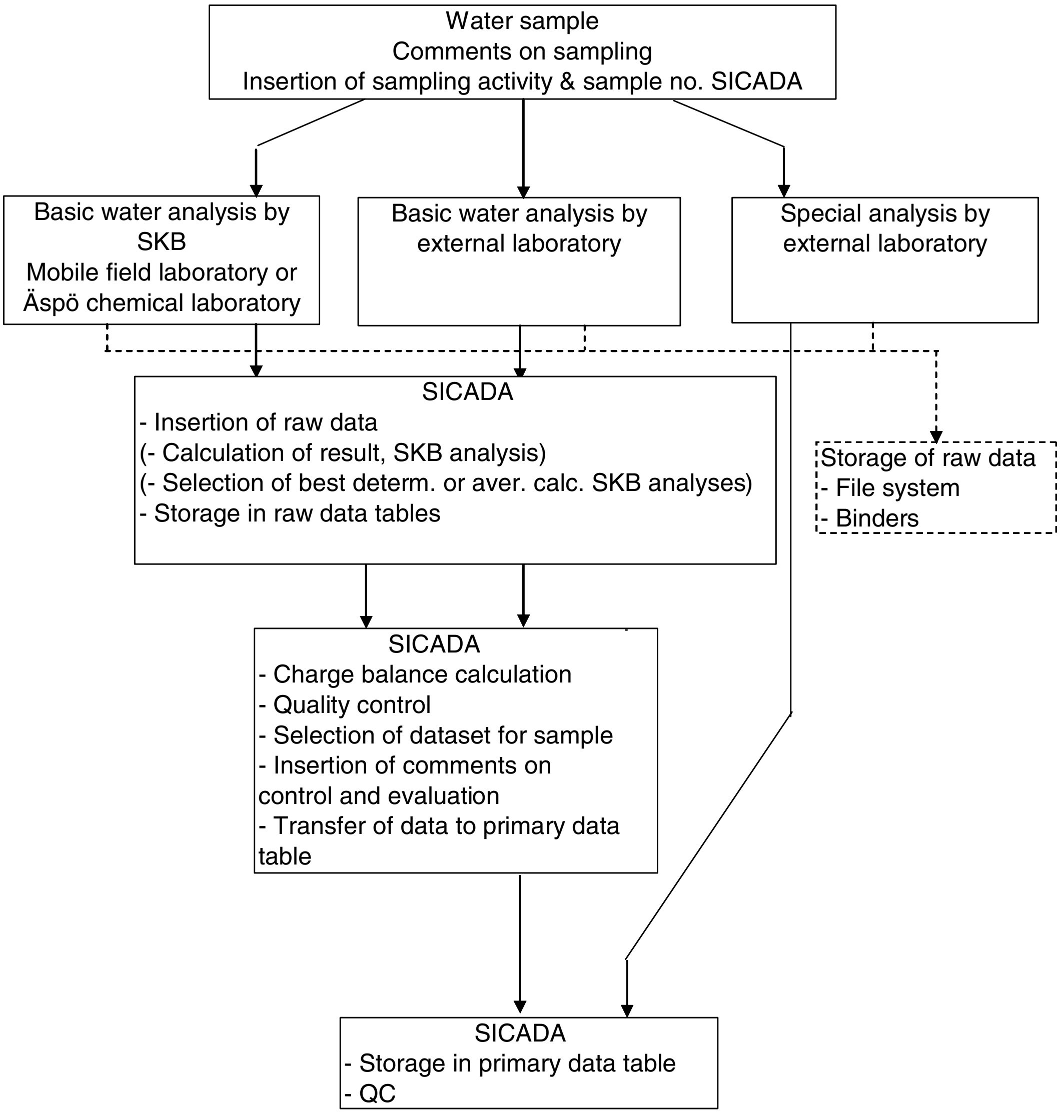


Figure 7-1. *Overview of data management for hydrogeochemical data.*

8 Results

8.1 Chemmac measurement data

The Chemmac measurement in the first section 230.5- 237.6 m was interrupted twice due to a pump failure and the two continuous measurement periods lasted only about two weeks each. The redox measurements did not succeed and the pH measurements by the borehole Chemmac showed scattered and non-consistent values. A possible reason is corrosion reactions in the downhole equipment. Further, the oxygen measurement values were well above zero despite the fact that all iron was present as ferrous iron (Fe+II). Possible explanations might be electric disturbances, bad membrane in the oxygen probe, or oxygen intrusion into the surface Chemmac. The last reason would also explain the positive redox potential measured at the ground surface but it is not, however, consistent with the iron results. The measurement sequences of pH, electric conductivity, dissolved oxygen and water temperature for section 230.5- 237.6 m are plotted versus time in Appendix 5.

The redox measurements and the downhole pH measurements behaved very much in the same way in the second section 354.0-361.1 m. Also in this case severe corrosion was discovered when the equipment was lifted to the ground surface after the measurement period. However, measured dissolved oxygen was below the detection limit. The measurement sequences of Eh, pH, electric conductivity, dissolved oxygen and water temperature for section 354.0-361.1 m are plotted versus time in Appendix 6.

The measurement data sequences were evaluated in order to obtain one representative value of pH, electric conductivity and dissolved oxygen for the borehole section as described in Section 7.1. Data were selected from a part of the measurement sequence where the electrodes showed stable values. The evaluated results from the measurements in the two sections are given in Table 8-1.

Table 8-1. Evaluated results from the Chemmac measurements in KFM04A.

Borehole section (m)	**Electric conductivity* (mS/m)**	**pH (surface Chemmac)****	**pH (borehole Chemmac)****	**Eh (borehole Chemmac)** (mV)**	**Dissolved oxygen*** (mg/L)**
230.5-237.6	1677 ± 20	7.36 ± 0.09	rejected	rejected	(0.18 ± 0.01)
354.0-361.1	1625 ± 20	7.33 ± 0.12	rejected	rejected	0.00 ± 0.01

* The electric conductivity is measured between 0-10 000 mS/m with a resolution of 1 % of the measurement interval.

** Evaluated result and measurement uncertainty calculated as described in Section 7.1.2.

*** Measurement interval 0-15 mg/L, resolution 0.01 mg/L.

8.2 Water analysis data

Basic water analyses as well as analyses of trace and rare earth metals and isotope determinations were performed on samples collected in the two sections 230.5-237.6 m and 354.0-361.1 m. Some of the analyses, especially the isotope determinations, take time and will not be available in time for the data freeze 1.2. Data that were available in SICADA at the printing date of this report are included in Appendix 8. The data sets will be completed later in a second version of the report.

The basic water analyses include the major constituents Na, K, Ca, Mg, S, SO_4^{2-}, Cl^-, Si and HCO_3^- as well as the minor constituents Fe, Li, Mn, DOC, Br, F, HS^- and NH_4^+. Furthermore, batch measurements of pH and electric conductivity are included. Another important parameter is the flushing water content in each sample. The basic water analytical data and relative charge balance errors are compiled in Appendix 8, Table A8-1. Existing batch measurement values of pH and/or electric conductivity are compared to the corresponding on-line Chemmac measurement values for section 230.5-237.6 m in Appendix 5. The charge balance errors give an indication of the quality and uncertainty of the analyses of major constituents. The error exceeds the acceptable level of ± 5 % in one case, probably due to an erroneously high sodium concentration value.

The flushing water content should not exceed 1% in a sample considered representative for the groundwater of the sampled fracture zone. This condition was, however, not met in the two sections investigated in KFM04A (uncertain value between 7 and 15 % in both sections). The flushing water content in the samples is calculated using the nominal Uranine concentration (0.2 mg/L) in the flushing water to give the low value. If the average Uranine concentration is used, the higher percentage is obtained.

Analyses of trace and rare earth metals include U, Th, Sc, Rb, Y, Zr, In, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Commonly occurring metals, such as Cu, Zn, Pb and Mo, are not included in the analysis programme due to contamination considerations. The trace element data are compiled in Appendix 8, Table A8-3.

The isotope determinations include the stable isotopes δD, $\delta^{18}O$, $^{10}B/^{11}B$, $\delta^{34}S$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ as well as the radioactive isotopes Tr (TU), ^{14}C (pmC), ^{238}U, ^{235}U, ^{234}U, ^{232}Th, ^{230}Th, ^{226}Ra and ^{222}Rn. The isotope data are presented in Appendix 8, Table A8-2 and Table A8-4.

9 Summary and discussion

The chemical characterisation of the two sections in borehole KFM04A is far from complete. Several special sampling methods were not conducted due to high flushing water content and lack of reliable redox measurements. Further, three lowerings/liftings of the downhole equipment were made and severe corrosion damage was discovered at all three lifting occasions. The downhole units were changed between each run. The electric conditions seem to be different in this borehole compared to previously investigated boreholes within the investigation area and a special investigation has been initiated in order to find out what causes the corrosion. The limited results from the borehole include water analyses and a reduced number of Chemmac parameters. The results are summarized bellow:

- No reliable redox potential data were obtained in the borehole. Further, pH measured by the borehole Chemmac was erroneous. A probable reason for the erroneous redox potential and pH measurements in the borehole Chemmac could be the corrosion reactions in the downhole equipment. The positive redox potential measured by the surface Chemmac may also be caused by air intrusion. The pH values measured in the surface cell appear to be reliable.
- Iron is present as ferrous iron at unusually high concentration in both sections. It cannot be excluded that the high iron concentration is caused by the corrosion reactions. Further, the iron concentrations determined by ICP technique are even higher, indicating the presence of colloidal iron.
- The calculated flushing water content in the samples is uncertain due to irregular dosing of Uranine to the flushing water during the drilling. However, the presented flushing water contents in Appendix 8 are underestimated rather than over-estimated.
- An upper limit for the allowed flushing water content in a representative water sample is set to 1 %. This condition was not met. The flushing water contents in the final samples amounts to between 6 % and 15 % in both sections.

10 References

/1/ **SKB, 2001.** Site investigations. Investigation methods and general execution programme. SKB TR-01-29, Svensk Kärnbränslehantering AB.

/2/ **Claesson L-Å, Nilsson G, 2004.** Forsmark site investigation. Drilling of the telescopic borehole KFM04A and the percussion drilled borehole KFM04B at drilling site DS4. SKB P-04-xx (in progress), Svensk Kärnbränslehantering AB.

/3/ **Claesson L-Å, Nilsson G, 2004.** Forsmark site investigation. Drilling of a flushing water well, HFM10, a groundwater monitoring well, HFM09, and a groundwater monitoring well in soil, SFM0057, at drillsite DS4. SKB P-04-76, Svensk Kärnbränslehantering AB.

/4/ **Nilsson Daniel, 2004.** Forsmark site investigation. Sampling and analyses of groundwater in percussion drilled boreholes. Results from the percussion boreholes HFM09 to HFM19 and the percussion drilled part of KFM06A. SKB P-03-xx, Svensk Kärnbränslehantering AB.

/5/ **Pedersen K, Kalmus A, 2003.** Forsmark site investigation. Control of microorganism content in flushing water used for drilling of KFM02A and KFM04A. SKB P-03-92, Svensk Kärnbränslehantering AB.

/6/ **Berg C, Nilsson A-C, 2004.** Forsmark site investigation. Hydrochemical logging in KFM04A. SKB P-04-47**,** Svensk Kärnbränslehantering AB.

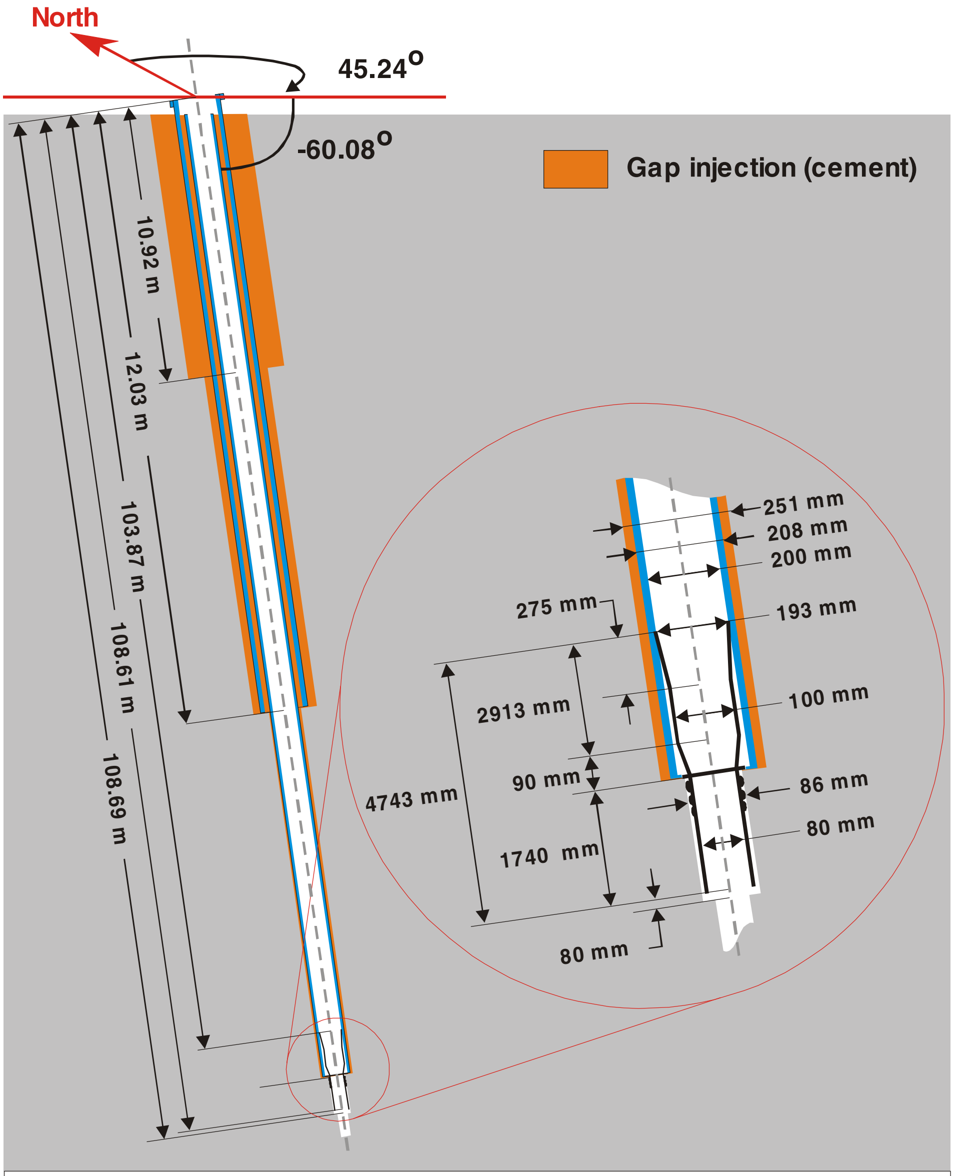
/7/ **Rouhiainen P, Pöllänen J, 2004.** Forsmark site investigation. Difference flow logging. Borehole KFM04A. SKB P-04-xx (in progress), Svensk Kärnbränslehantering AB.

Appendix 1

Design of cored borehole KFM04A

Technical data

Borehole KFM04A



Drilling reference point

Northing:	6698921.74	(m), RT90 2,5 gon V 0:-15
Easting:	1630978.96	(m), RT90 2,5 gon V 0:-15
Elevation:	8.77	(m), RHB70

Drilling period

Drilling start date:	2003-05-20
Drilling stop date:	2003-11-19

Borehole

Lenght:	1001.42 m

Appendix 2

Results of difference flow logging in KFM04A

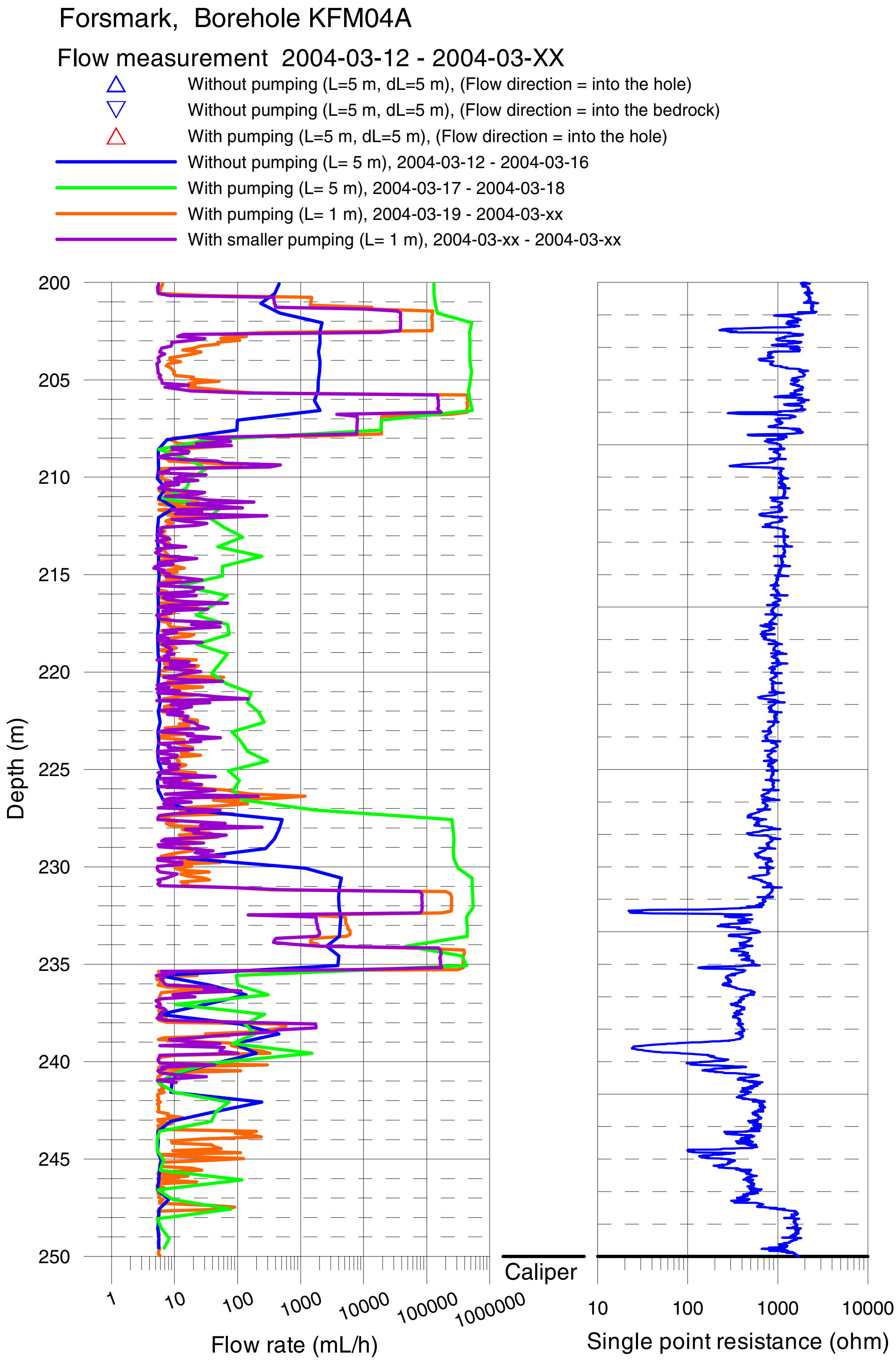


Figure A2-1. *Borehole KFM04A: Differential flow measurements from 200-250 m including the water bearing fracture zone at 230 m /7/.*

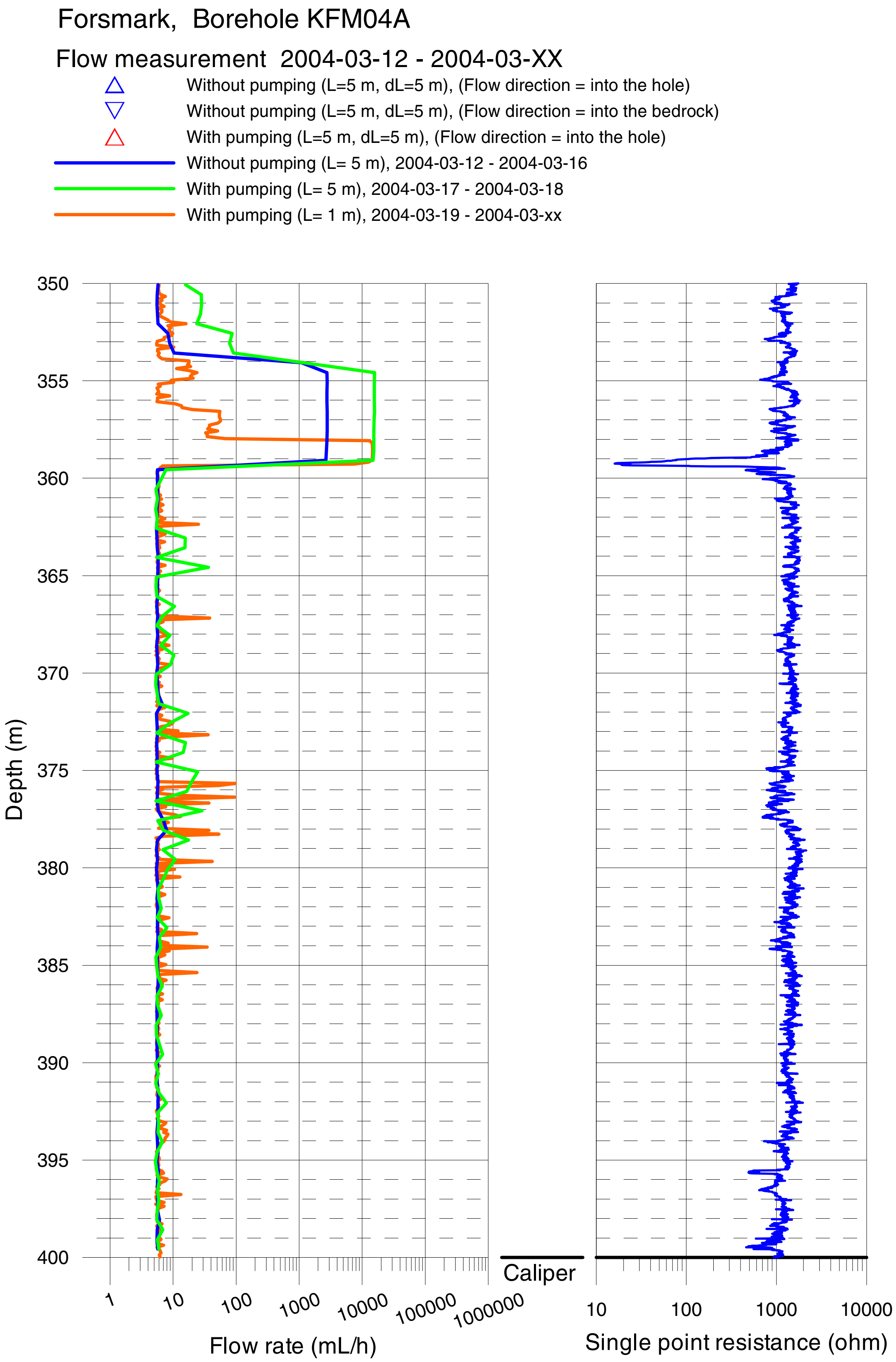
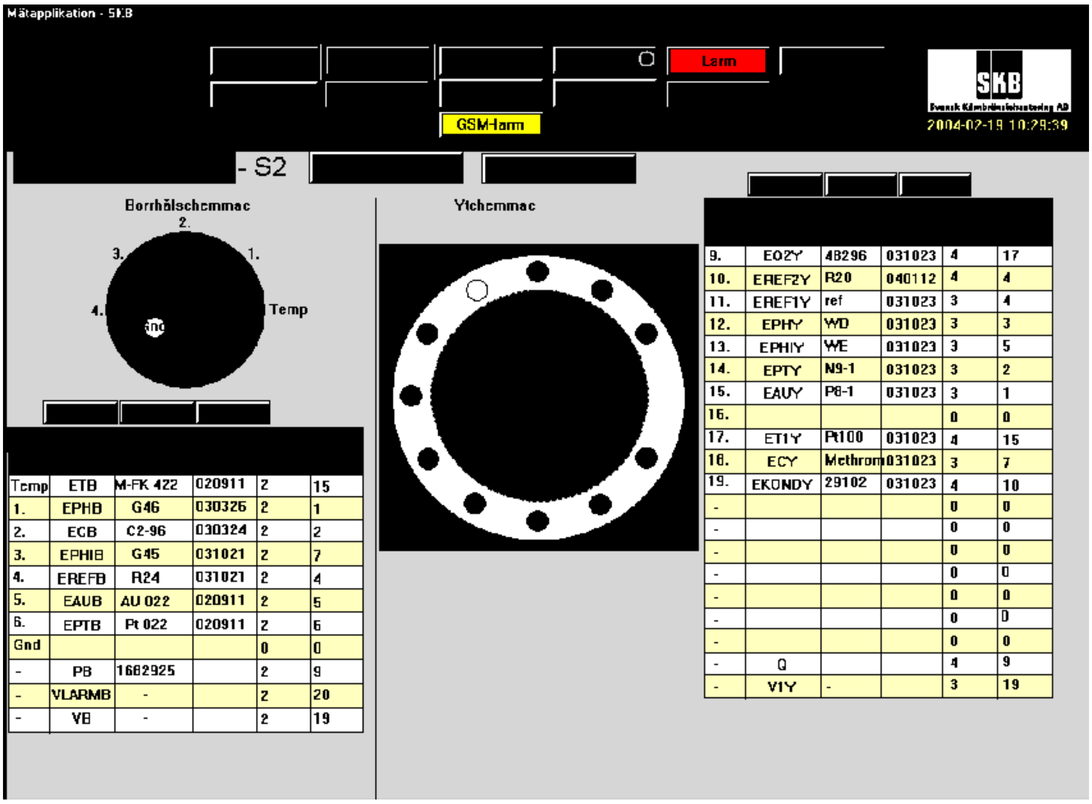


***Figure A2-2.** Borehole KFM04A: Differential flow measurements from 350-400 m including the water bearing fracture zone at 354 m /7/.*

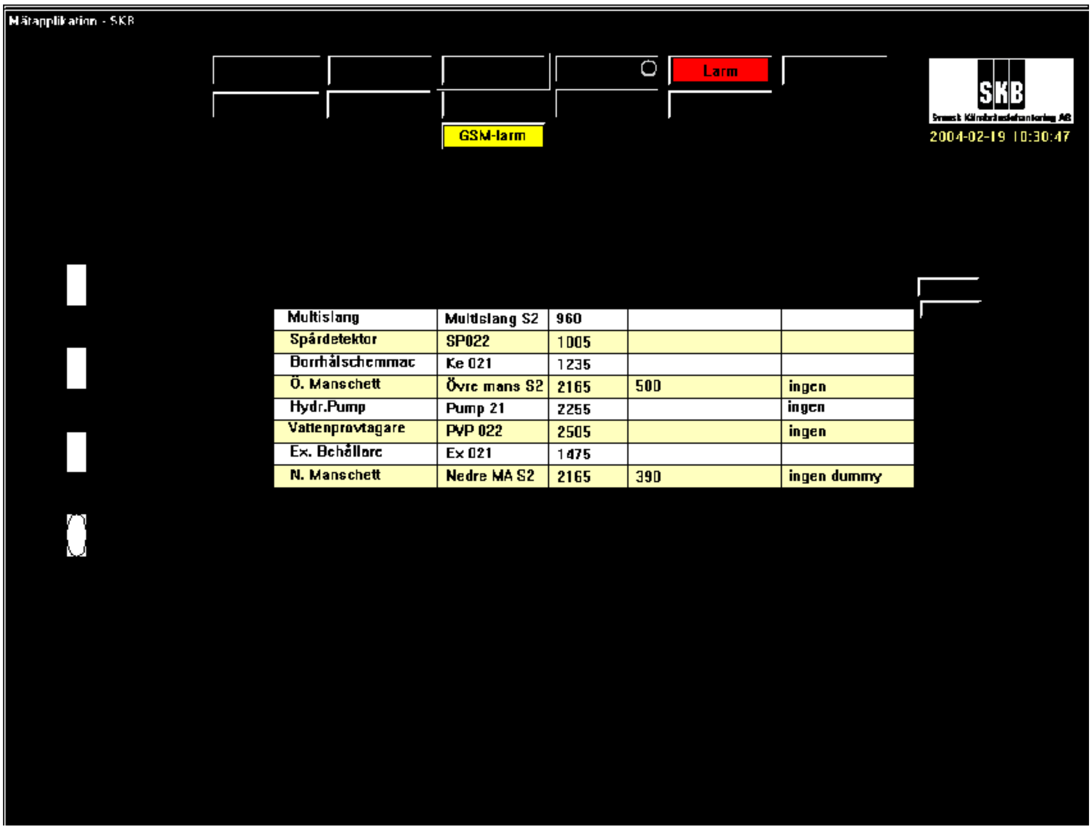
Measurement information



Temp	ETB	M-FK 422	020911	2	15
1.	EPHB	G46	030326	2	1
2.	ECB	C2-96	030324	2	2
3.	EPHIB	G45	031021	2	7
4.	EREFB	R24	031021	2	4
5.	EAUB	AU 022	020911	2	5
6.	EPTB	Pt 022	020911	2	6
Gnd				0	0
-	PB	1682925		2	9
-	VLARMB	-		2	20
-	VB	-		2	19

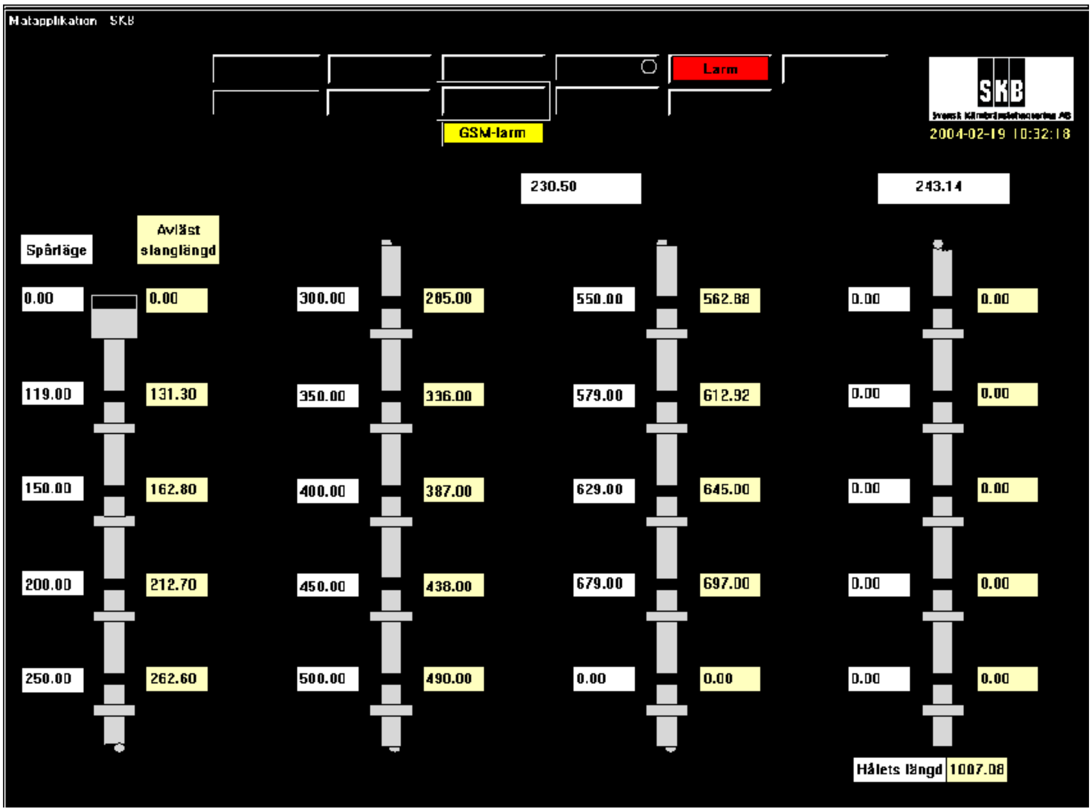
9.	EO2Y	48296	031023	4	17
10.	EREF2Y	R20	040112	4	4
11.	EREF1Y	ref	031023	3	4
12.	EPHY	WD	031023	3	3
13.	EPHIY	WE	031023	3	5
14.	EPTY	N9-1	031023	3	2
15.	EAUY	P8-1	031023	3	1
16.				0	0
17.	ET1Y	Pt100	031023	4	15
18.	ECY	Methrom	031023	3	7
19.	EKONDY	29102	031023	4	10
-				0	0
-				0	0
-				0	0
-				0	0
-				0	0
-				0	0
-				0	0
-	Q			4	9
-	V1Y	-		3	19

Figure A3-1. *Electrode configuration KFM04A, section 230.5-237.6 m.*



Multislang	Multislang S2	960		
Spårdetektor	SP022	1005		
Borrhålschemmac	Ke 021	1235		
Ö. Manschett	Övre mans S2	2165	500	ingen
Hydr.Pump	Pump 21	2255		ingen
Vattenprovtagare	PVP 022	2505		ingen
Ex. Behållare	Ex 021	1475		
N. Manschett	Nedre MA S2	2165	390	ingen dummy

Figure A3-2. *Configuration of downhole equipment KFM04A, section 230.5-237.6 m.*



2004-02-19 10:32:18

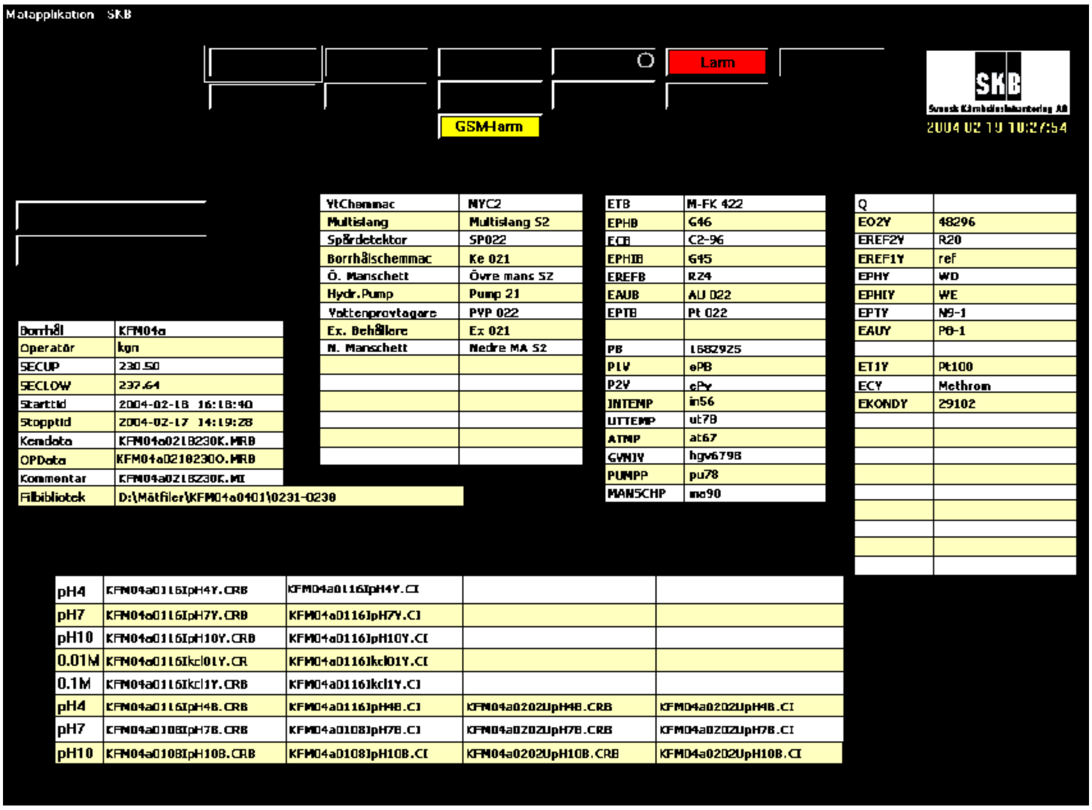
230.50

243.14

Spårläge	Avläst slanglängd						
0.00	0.00	300.00	285.00	550.00	562.88	0.00	0.00
119.00	131.30	350.00	336.00	579.00	612.92	0.00	0.00
150.00	162.80	400.00	387.00	629.00	645.00	0.00	0.00
200.00	212.70	450.00	438.00	679.00	697.00	0.00	0.00
250.00	262.60	500.00	490.00	0.00	0.00	0.00	0.00

Hålets längd 1007.08

***Figure A3-3.** Length calibration KFM04A, section 230.5-237.6 m.*



2004 02 19 10:27:54

Borrhål	KFM04a
Operatör	kgn
SECUP	230.50
SECLOW	237.64
Starttid	2004-02-18 16:18:40
Stopptid	2004-02-17 14:19:28
Kemdata	KFM04a0218230K.MRB
OPData	KFM04a02182300.MRB
Kommentar	KFM04a0218230K.MI
Filbibliotek	D:\Mätfiler\KFM04a0401\0231-0230

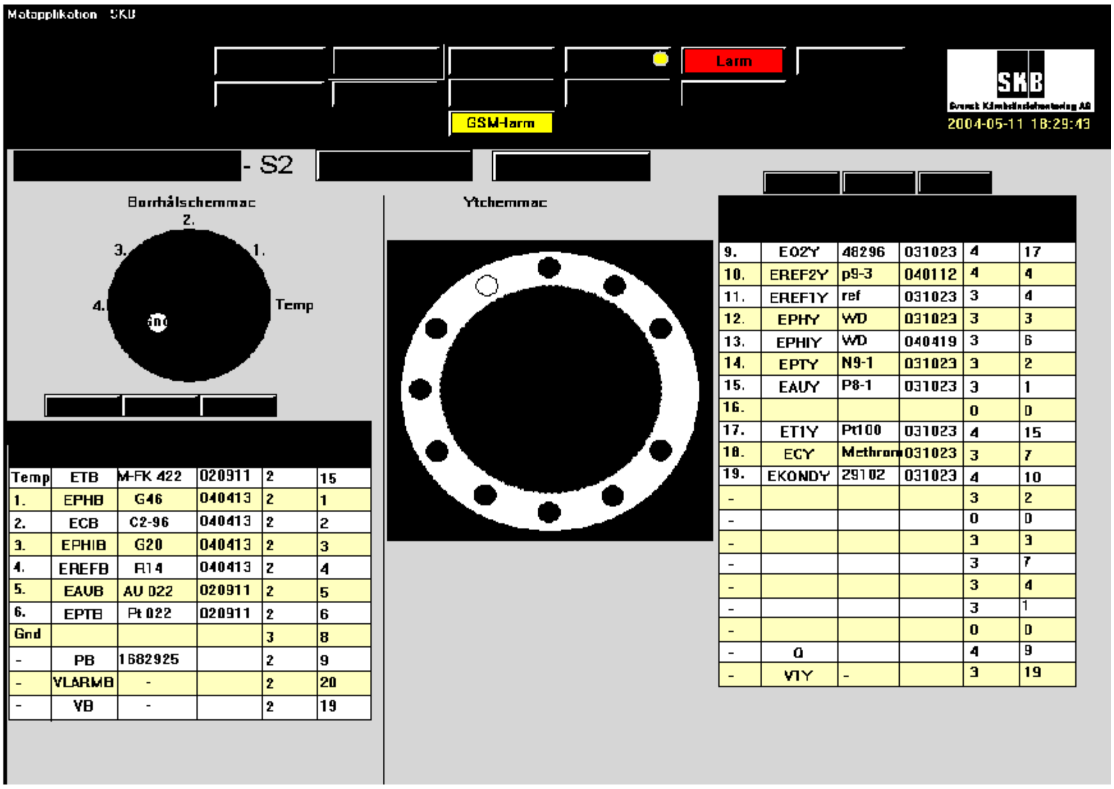
YtChemmac	MYC2
Multislang	Multislang S2
Spårdetektor	SP022
Borrhålschemmac	Ke 021
Ö. Manschett	Övre mans S2
Hydr.Pump	Pump 21
Vattenprovtagare	PVP 022
Ex. Behållare	Ex 021
N. Manschett	Nedre MA S2

ETB	M-FK 422
EPHB	G46
ECB	C2-96
EPHIB	G45
EREFB	R24
EAUB	AU 022
EPTB	Pt 022
PB	1682925
P1V	ePB
P2V	cPv
INTEMP	in56
UTTEMP	ut78
ATMP	at67
GVNIV	hgv6798
PUMPP	pu78
MANSCHP	ma90

Q	
EO2Y	48296
EREF2Y	R20
EREF1Y	ref
EPHY	WD
EPHIY	WE
EPTY	N9-1
EAUY	P8-1
ET1Y	Pt100
ECY	Methrom
EKONDY	29102

pH4	KFM04a0116IpH4Y.CRB	KFM04a0116IpH4Y.CI		
pH7	KFM04a0116IpH7Y.CRB	KFM04a0116IpH7Y.CI		
pH10	KFM04a0116IpH10Y.CRB	KFM04a0116IpH10Y.CI		
0.01M	KFM04a0116Ikcl01Y.CR	KFM04a0116Ikcl01Y.CI		
0.1M	KFM04a0116Ikcl1Y.CRB	KFM04a0116Ikcl1Y.CI		
pH4	KFM04a0116IpH4B.CRB	KFM04a0116IpH4B.CI	KFM04a0202UpH4B.CRB	KFM04a0202UpH4B.CI
pH7	KFM04a0108IpH7B.CRB	KFM04a0108IpH7B.CI	KFM04a0202UpH7B.CRB	KFM04a0202UpH7B.CI
pH10	KFM04a0108IpH10B.CRB	KFM04a0108IpH10B.CI	KFM04a0202UpH10B.CRB	KFM04a0202UpH10B.CI

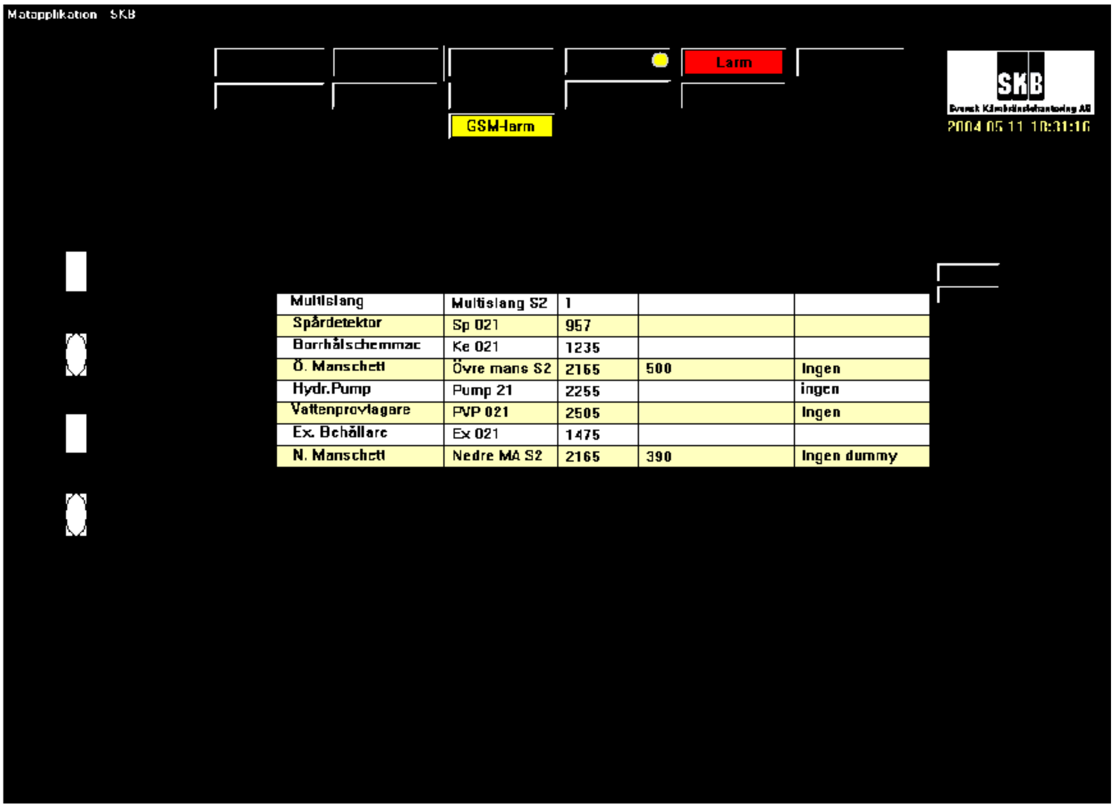
***Figure A3-4.** Administration KFM04A, section 230.5-237.6 m.*



Temp	ETB	M-FK 422	020911	2	15
1.	EPHB	G46	040413	2	1
2.	ECB	C2-96	040413	2	2
3.	EPHIB	G20	040413	2	3
4.	EREFB	R14	040413	2	4
5.	EAVB	AU 022	020911	2	5
6.	EPTB	Pt 022	020911	2	6
Gnd				3	8
-	PB	1682925		2	9
-	VLARMB	-		2	20
-	VB	-		2	19

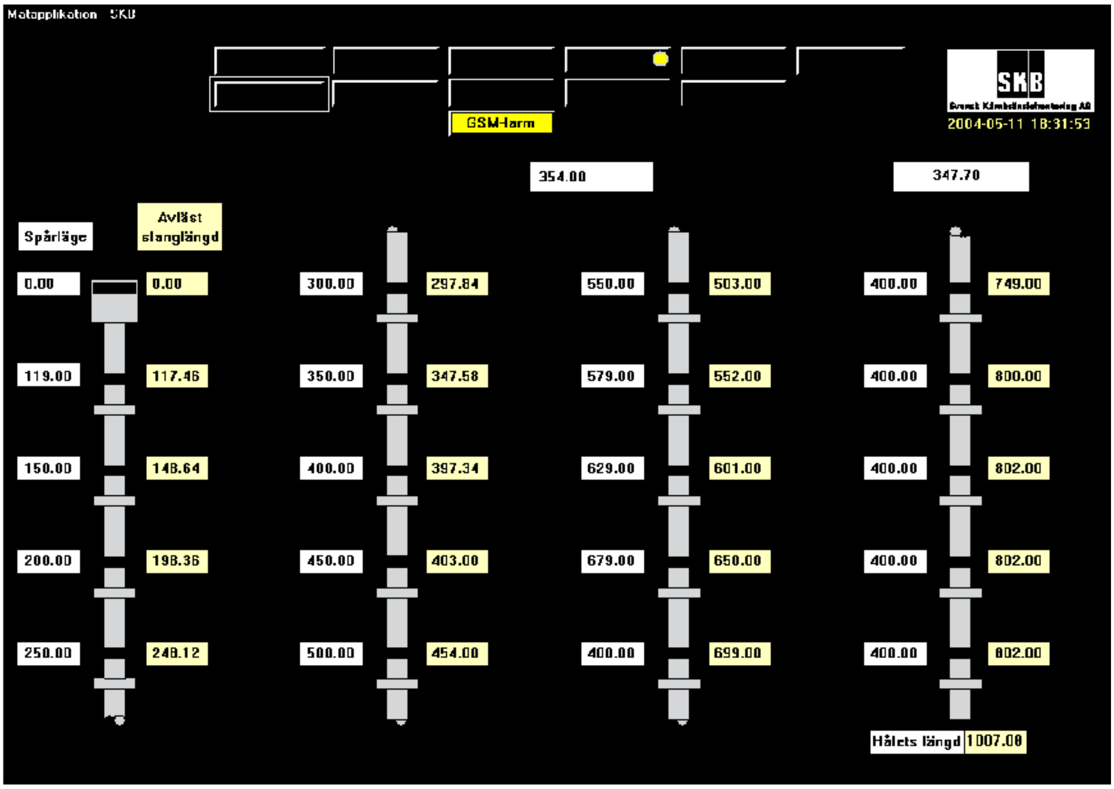
9.	EO2Y	48296	031023	4	17
10.	EREF2Y	p9-3	040112	4	4
11.	EREF1Y	ref	031023	3	4
12.	EPHY	WD	031023	3	3
13.	EPHIY	WD	040419	3	6
14.	EPTY	N9-1	031023	3	2
15.	EAUY	P8-1	031023	3	1
16.				0	0
17.	ET1Y	Pt100	031023	4	15
18.	ECY	Methrom	031023	3	7
19.	EKONDY	29102	031023	4	10
-				3	2
-				0	0
-				3	3
-				3	7
-				3	4
-				3	1
-				0	0
-	Q			4	9
-	V1Y	-		3	19

__Figure A3-5.__ Electrode configuration KFM04A, section 354.0-361.1 m.



Multislang	Multislang S2	1		
Spårdetektor	Sp 021	957		
Borrhålschemmac	Ke 021	1235		
Ö. Manschett	Övre mans S2	2165	500	Ingen
Hydr.Pump	Pump 21	2255		ingen
Vattenprovtagare	PVP 021	2505		Ingen
Ex. Behållare	Ex 021	1475		
N. Manschett	Nedre MA S2	2165	390	Ingen dummy

__Figure A3-6.__ Configuration of downhole equipment KFM04A, section 354.0-361.1 m.



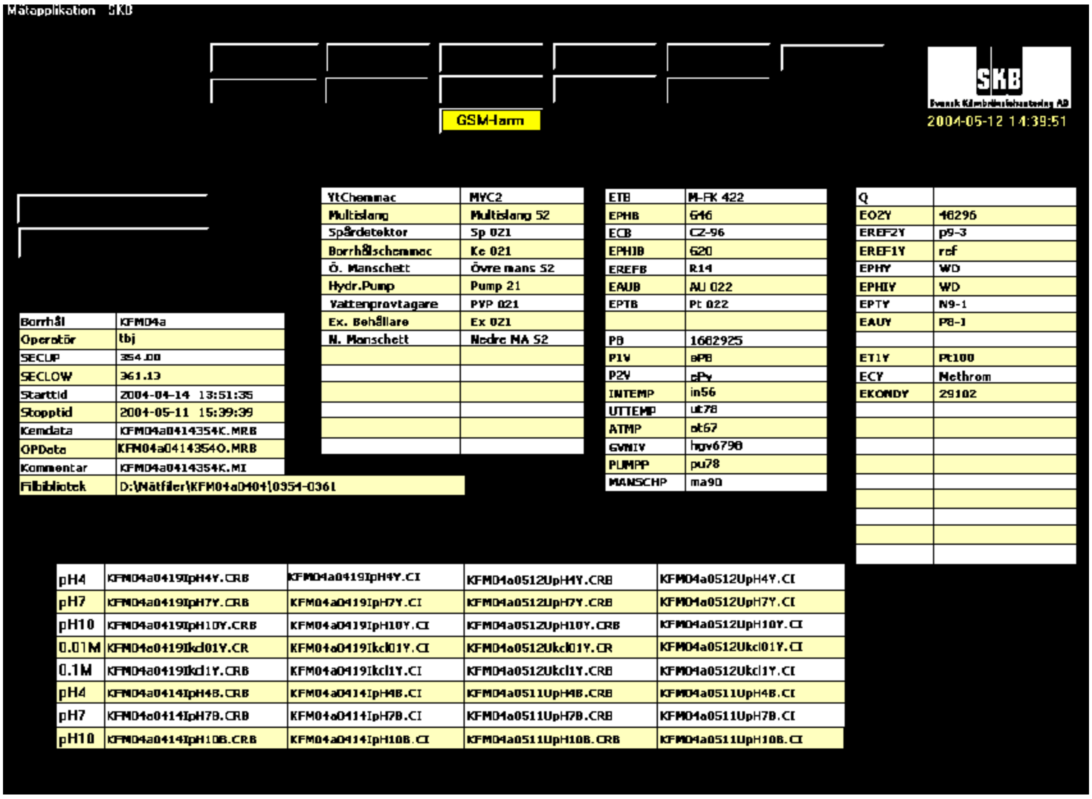
354.00

347.70

Spårläge	Avläst slanglängd						
0.00	0.00	300.00	297.84	550.00	503.00	400.00	749.00
119.00	117.46	350.00	347.58	579.00	552.00	400.00	800.00
150.00	148.64	400.00	397.34	629.00	601.00	400.00	802.00
200.00	198.36	450.00	403.00	679.00	650.00	400.00	802.00
250.00	248.12	500.00	454.00	400.00	699.00	400.00	802.00

Hålets längd 1007.08

Figure A3-7. Length calibration KFM04A, section 354.0-361.1 m.



Borrhål	KFM04a
Operatör	tbj
SECUP	354.00
SECLOW	361.13
Starttid	2004-04-14 13:51:35
Stopptid	2004-05-11 15:39:39
Kemdata	KFM04a0414354K.MRB
OPData	KFM04a0414354O.MRB
Kommentar	KFM04a0414354K.MI
Filbibliotek	D:\Mätfiler\KFM04a0404\0354-0361

YtChemmac	MYC2
Multislang	Multislang 52
Spårdetektor	Sp 021
Borrhålschemmac	Ke 021
Ö. Manschett	Övre mans 52
Hydr.Pump	Pump 21
Vattenprovtagare	PVP 021
Ex. Behållare	Ex 021
N. Manschett	Nedre MA 52

ETB	M-FK 422
EPHB	646
ECB	CZ-96
EPHIB	620
EREFB	R14
EAUB	AU 022
EPTB	Pt 022
PB	1682925
P1V	aPB
P2V	cPv
INTEMP	in56
UTTEMP	ut78
ATMP	at67
GVNIV	hgv6798
PUMPP	pu78
MANSCHP	ma90

Q	
EO2Y	48296
EREF2Y	p9-3
EREF1Y	ref
EPHY	WD
EPHIY	WD
EPTY	N9-1
EAUY	P8-1
ET1Y	Pt100
ECY	Methrom
EKONDY	29102

pH4	KFM04a0419IpH4Y.CRB	KFM04a0419IpH4Y.CI	KFM04a0512UpH4Y.CRB	KFM04a0512UpH4Y.CI
pH7	KFM04a0419IpH7Y.CRB	KFM04a0419IpH7Y.CI	KFM04a0512UpH7Y.CRB	KFM04a0512UpH7Y.CI
pH10	KFM04a0419IpH10Y.CRB	KFM04a0419IpH10Y.CI	KFM04a0512UpH10Y.CRB	KFM04a0512UpH10Y.CI
0.01M	KFM04a0419Ikcl01Y.CR	KFM04a0419Ikcl01Y.CI	KFM04a0512Ukcl01Y.CR	KFM04a0512Ukcl01Y.CI
0.1M	KFM04a0419Ikcl1Y.CRB	KFM04a0419Ikcl1Y.CI	KFM04a0512Ukcl1Y.CRB	KFM04a0512Ukcl1Y.CI
pH4	KFM04a0414IpH4B.CRB	KFM04a0414IpH4B.CI	KFM04a0511UpH4B.CRB	KFM04a0511UpH4B.CI
pH7	KFM04a0414IpH7B.CRB	KFM04a0414IpH7B.CI	KFM04a0511UpH7B.CRB	KFM04a0511UpH7B.CI
pH10	KFM04a0414IpH10B.CRB	KFM04a0414IpH10B.CI	KFM04a0511UpH10B.CRB	KFM04a0511UpH10B.CI

Figure A3-8. Administration KFM04A, section 354.0-361.1 m.

Appendix 4

Flow and pressure measurements

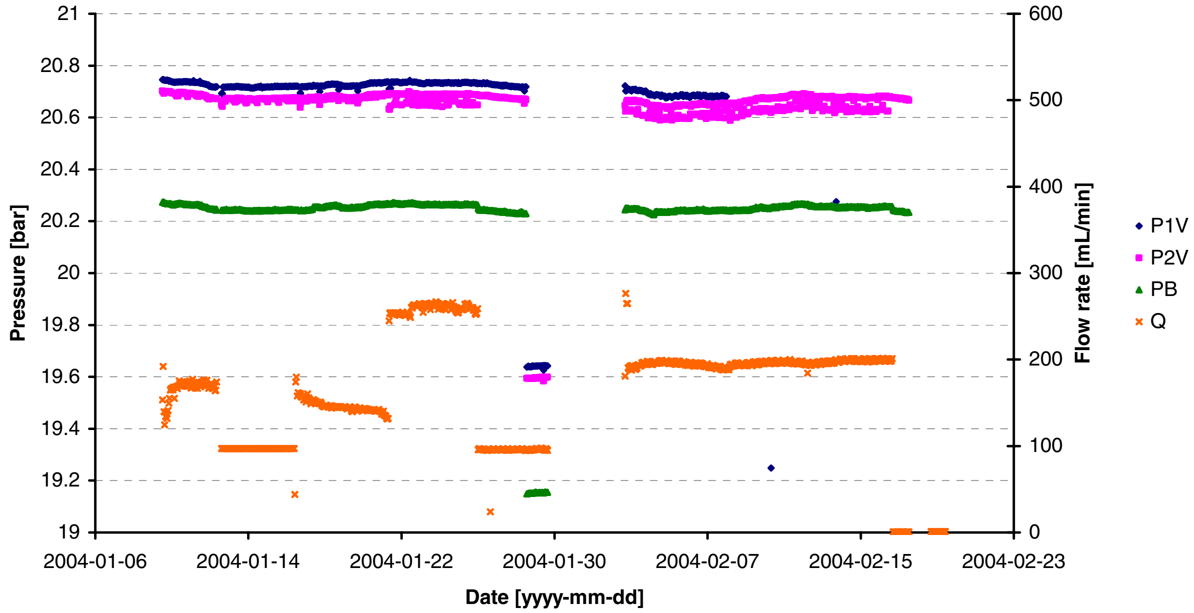


***Figure A4-1.** Pressure measured within the section (P1V, P2V), above the section (PB) and pumping flow rate (Q) from borehole section 230.5-237.6 m.*

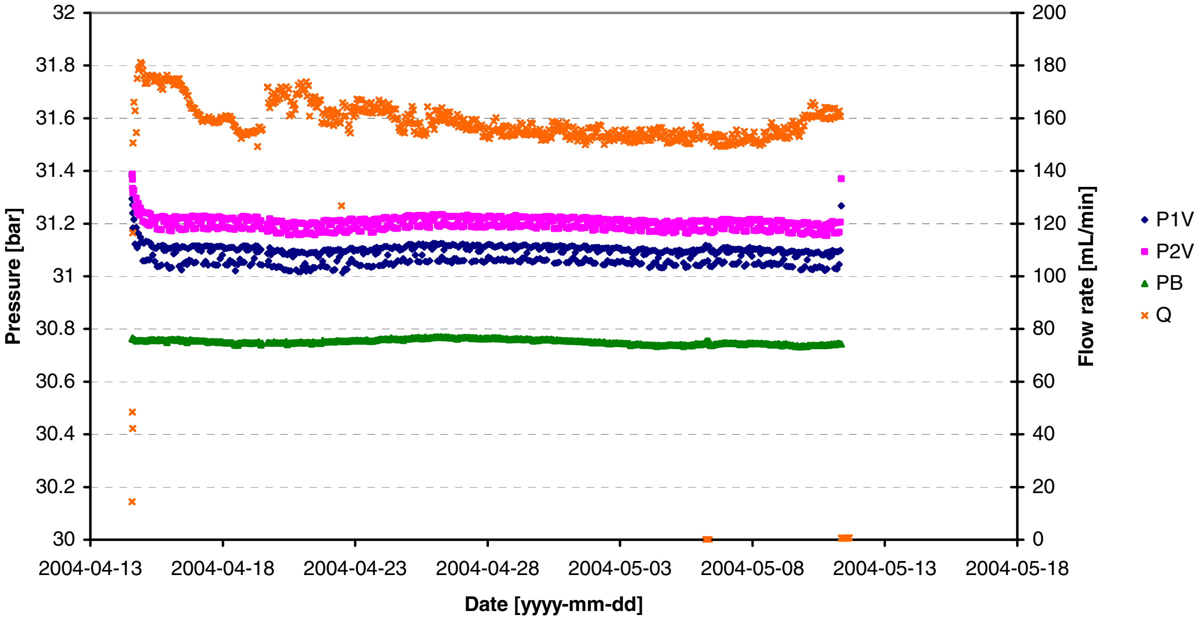


***Figure A4-2.** Pressure measured within the section (P1V, P2V), above the section (PB) and pumping flow rate (Q) from borehole section 354.0-361.1 m.*

Appendix 5

Chemmac measurements (pH, electric conductivity, dissolved oxygen and temperature), section 230.5-237.6 m

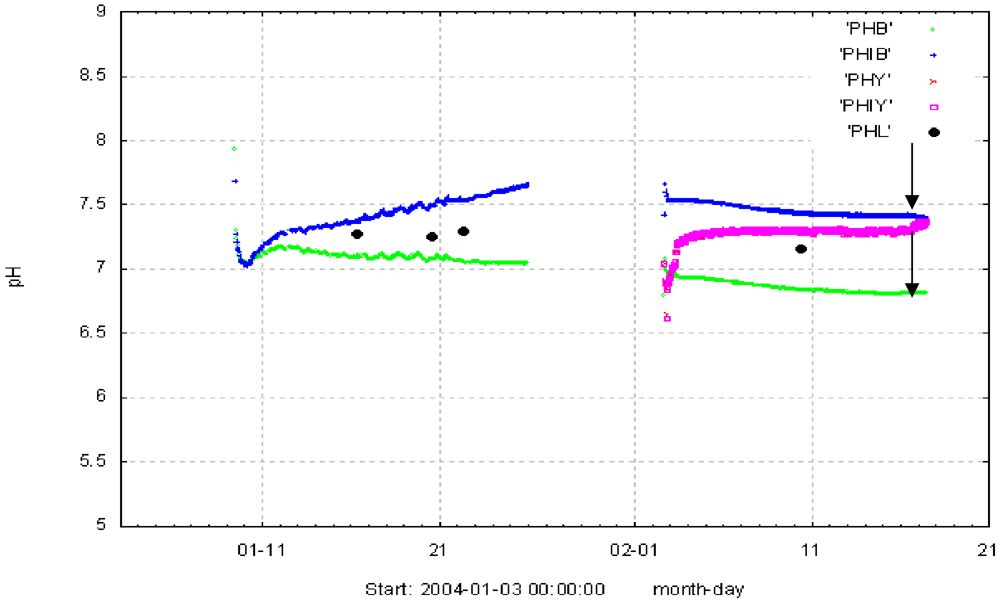


Figure A5-1. *Measurements of pH by two glass electrodes in the borehole section (PHB, PHIB) and two glass electrodes at the surface (PHY, PHIY). PHY and PHIY coincide/fall together. The laboratory pH in each collected sample (PHL) is given for comparison. The arrow shows the chosen representative pH values for the borehole section.*

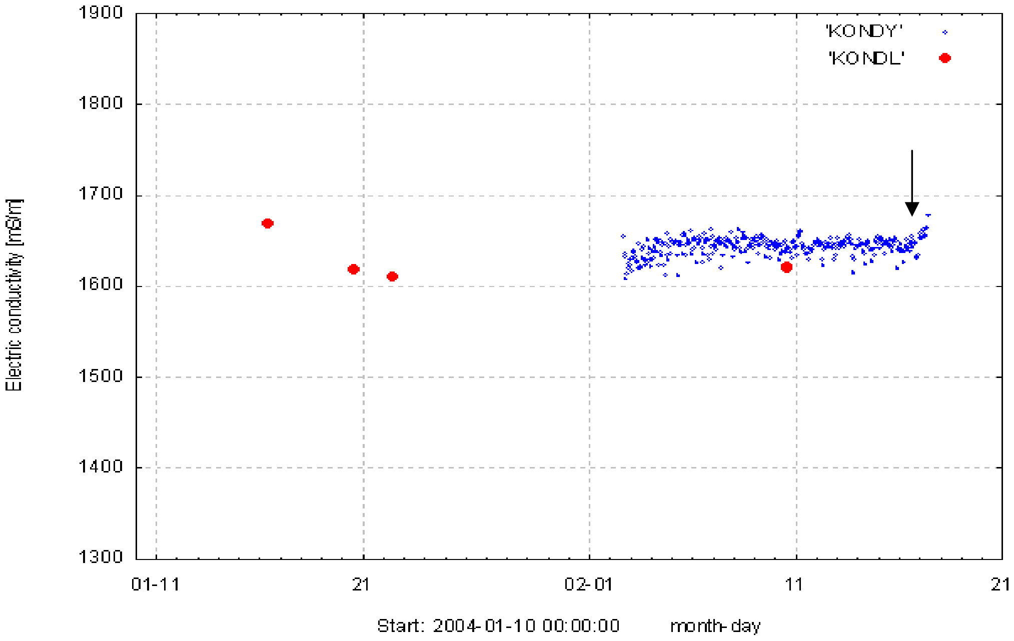


Figure A5-2. *Electric conductivity measurement in the surface measurement cell (KONDY). The first part of the measurement data was omitted since the water flow was affected by ice formation. The laboratory conductivity in each collected sample (KONDL) is given for comparison. The arrow shows the chosen representative electric conductivity value for the borehole section.*

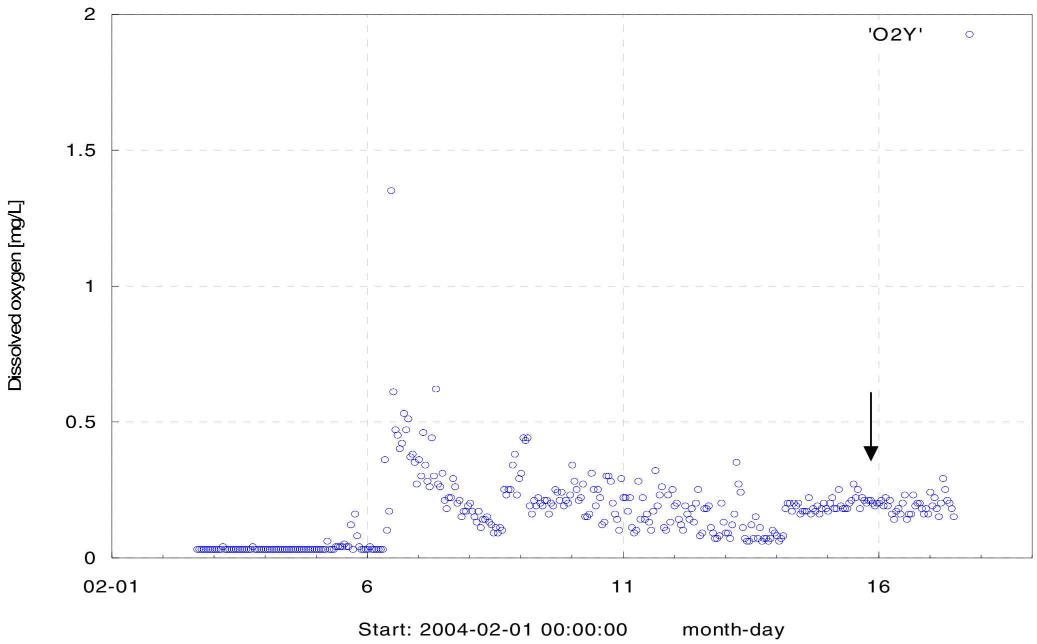


__Figure A5-3.__ Dissolved oxygen measurements (O2Y) in the surface measurement cell. The first part of the measurement data was omitted since the flow was affected by ice formation. The arrow shows the chosen representative value for dissolved oxygen in the borehole section.

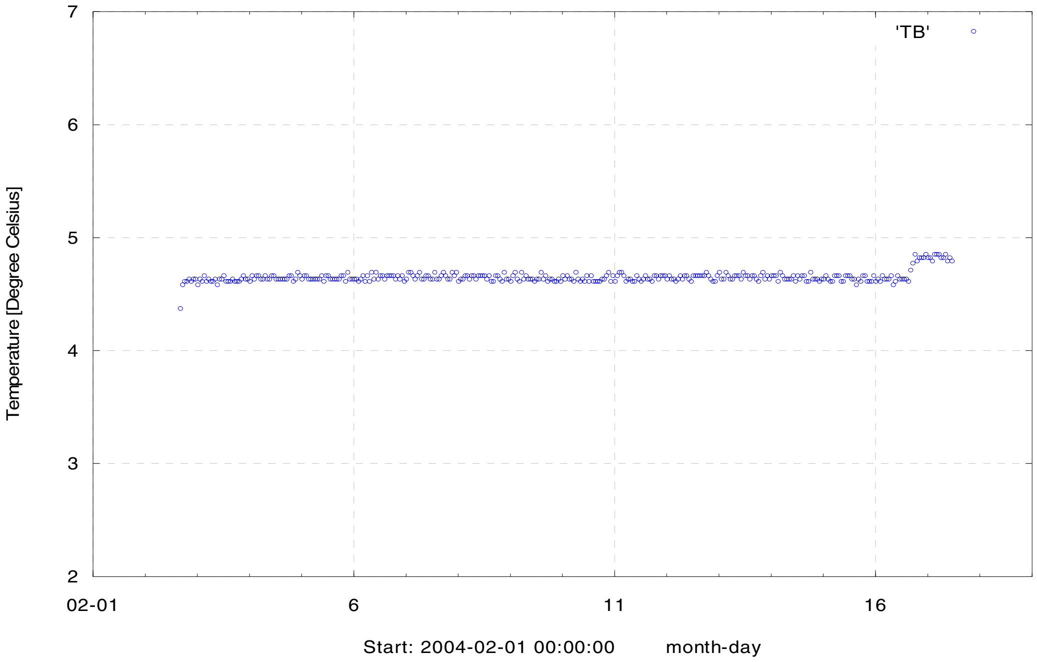


__Figure A5-4.__ Temperature of the groundwater in the borehole section (TB).

Appendix 6

Chemmac measurements (Eh, pH, electric conductivity, dissolved oxygen and temperature), section 354.0-361.1 m

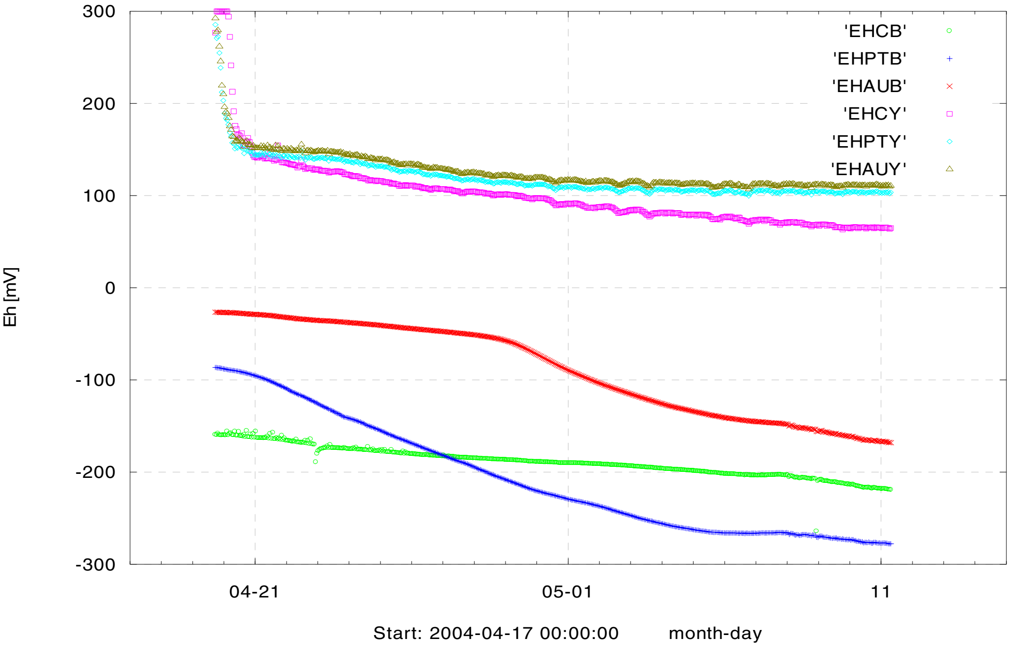


Figure A6-1. *Redox potential measurements (Eh) by platinum, gold and glassy carbon electrodes in the borehole section (EHPTB, EHAUB and EHCB) and at the surface (EHPTY, EHAUY and EHCY).*

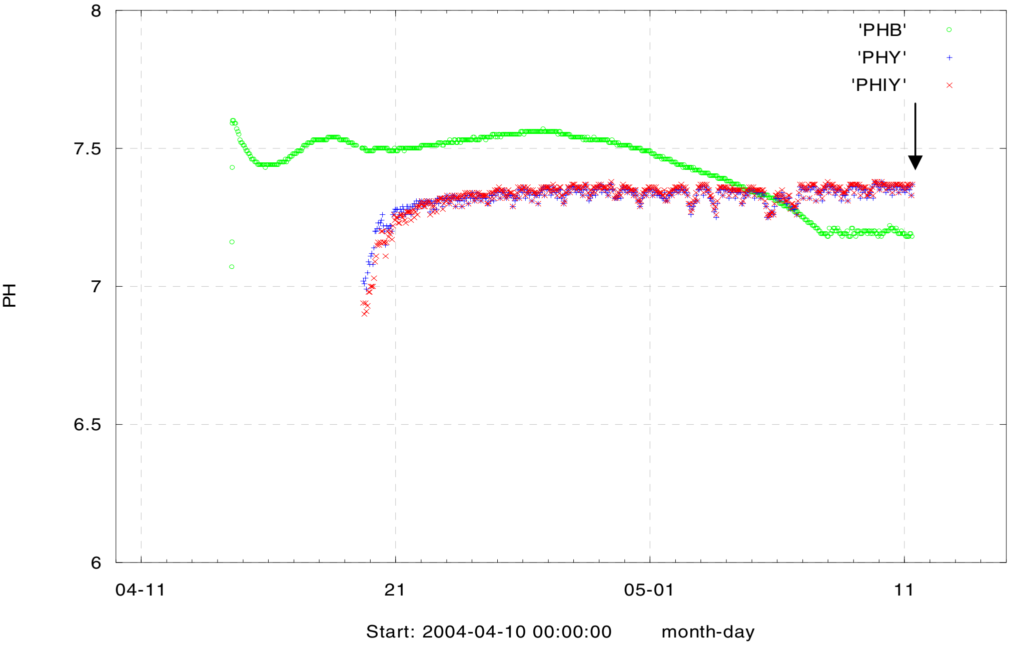


Figure A6-2. *Measurements of pH by a glass electrode in the borehole section (PHB) and two glass electrodes at the surface (PHY and PHIY). PHIB was omitted due to scattered values. The arrow shows the chosen representative pH values for the borehole section.*

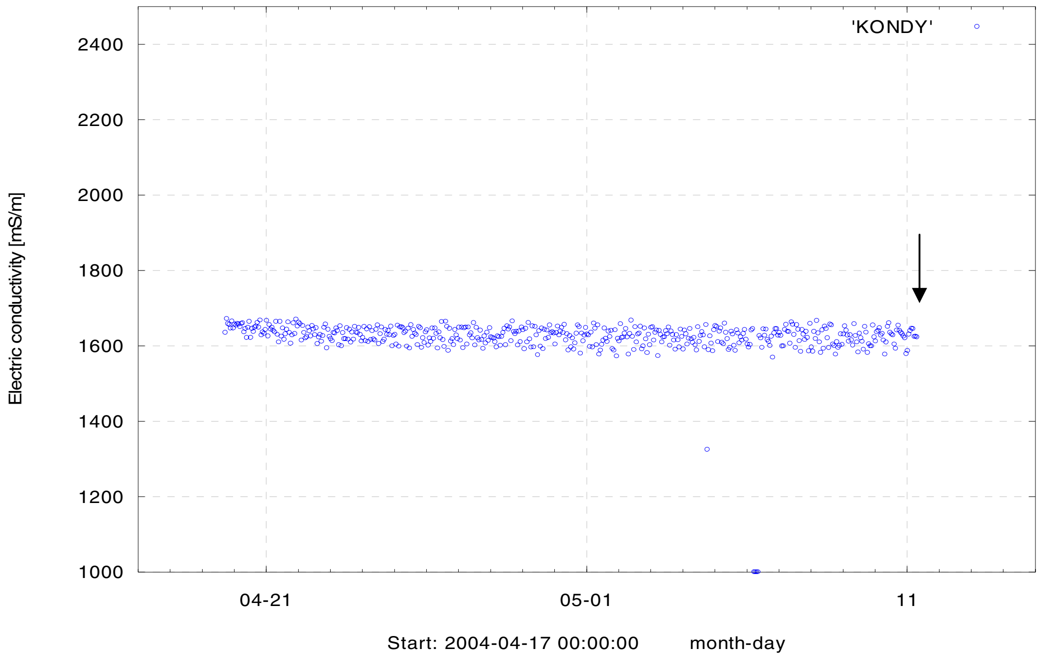


Figure A6-3. *Electric conductivity measurements in the surface measurement cell (KONDY). The arrow shows the chosen representative value for electric conductivity in the borehole section.*

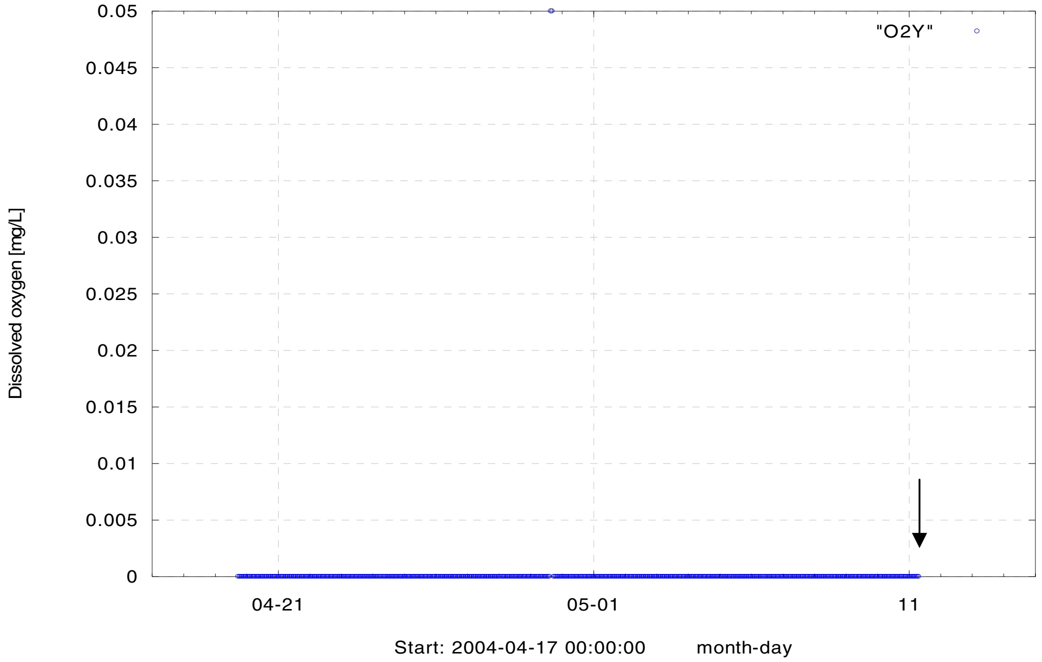


Figure A6-4. *Dissolved oxygen measurements (O2Y) in the surface measurement cell. The arrow shows the selected representative value for dissolved oxygen in the borehole section.*

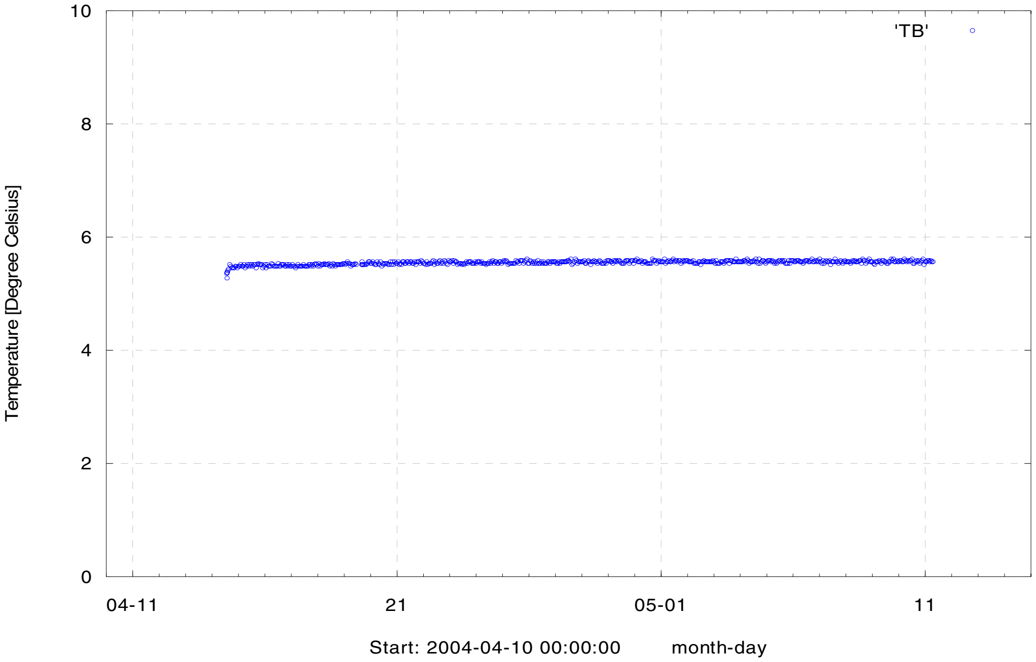


Figure A6-5. *Temperature of the groundwater in the borehole section (TB).*

Sampling and analysis methods

Table A7-1. Sample handling routines and analysis methods.

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Anions 1.	HCO_3 pH(lab) cond (lab)	Plastic	250	Yes (not in the field)	No	Titration Pot. meas, Cond. meas	Mobile field lab. AnalyCen	The same day – maximum 24 hours
Anions 2	Cl, SO_4, Br^-, F^-, I^-	Plastic	100	Yes (not in the field)	No	Titration (Cl^-) IC (Cl^-, SO4, Br^-, F^-) ISE (F^-)	Äspö:s chemistry lab. AnalyCen	Not critical (month)
	Br, I	Plastic	100	Yes (not in the field)	No	ICP MS	Paavo Ristola OY Analytica AB,	Not critical (month)
Cations, Si and S according to SKB class 3	Na, K, Ca, Mg, S(tot), Si(tot), Li, Sr	Plastic (at low conc. acid washed bottles)	100	Yes (not in the field)	Yes (not in the field, 1 mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AnalyCen	Not critical (month)
Cations, Si and S according to SKB class 4 and 5	Na, K, Ca, Mg, S(tot), Si(tot), Fe, Mn, Li, Sr	Plastic (Acid washed)	100	Yes (immediately in the field)	Yes (1mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AnalyCen	Not critical (month)
Fe(II), Fe(tot)	Fe(II), Fe(tot)	Plastic (Acid washed)	500	Yes	Yes (5 mL HCl))	Spectrophotometry Ferrozine method	Mobile field lab.	As soon as possible the same day
Hydrogen sulphide	HS^-	Glass (Winkler)	About 120×2	No	Ev 1 mL 1 M NaOH+ 1 mL 1M ZnAc	Spectrophotometry	AnalyCen Äspö:s chemistry lab.	Immediately or if conserved, a few days
Nutrient salts	NO_2, NO_3+NO_2, NH_4, PO_4	Plastic	250	No	No	Spectrophotometry	Äspö:s chemistry lab. AnalyCen	Maximum 24 hours
Environmental metals	Al, As, Ba, B, Cd, Co, Cr, Cu, Hg, Mo, Ni, P, Pb, V, Zn	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	Analytica AB, AnalyCen	Not critical (month)
Lantanoids, U, Th and so on.	Sc, Rb, Y, Zr, I, Sb, Cs, La, Hf, Tl, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, U, Th	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP-AES ICP-MS	SGAB Analytica, AnalyCen	Not critical (month)

Component group	**Component/ element**	**Sample container (material)**	**Volume (mL)**	**Filtering**	**Preparation/ Conservation***	**Analysis method**	**Laboratory*****	**Analysis within - or delivery time to lab.**
Dissolved organic Carbon, dissolved inorganic Carbon	DOC, DIC	Plastic	250 25	Yes	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time
Total organic Carbon	TOC	Plastic	250 25	No	Frozen, transported in isolated bag	UV oxidation, IR Carbon analysator Shimadzu TOC5000	Paavo Ristola OY Dept. of System ecology, SU	Short transportation time
Environmental isotopes	∂^{2}H, ∂^{18}O	Plastic	100	No	- -	MS	IFE	Not critical (month)
Tritium, Chlorine-37	^{3}H (enhanced.) ∂^{37}Cl	Plastic (dry bottle) Plastic	500 100	No No	- -	LSC ICP MS	Univ. of Waterloo	Not critical (month)
Carbon isotopes	∂^{13}C, pmC (^{14}C)	Glass (brown)	100×2	No	-	(A)MS	Univ. of Waterloo	A few days
Sulphur isotopes	∂^{34}S	Plastic	500 –1000	Yes	-	Combustion, ICP MS	IFE	No limit
Strontium-isotopes	^{87}Sr/^{86}Sr	Plastic	100	Yes	-	TIMS	IFE	Days or Week
Uranium and Thorium isotopes	^{234}U, ^{235}U, ^{238}U, ^{232} Th, ^{230}Th,	Plastic	50	No	-	Chemical separat. Alfa/gamma spectrometry	IFE SUERC	No limit
Boron isotopes	^{10}B/^{11}B	Plastic	100	Yes	Yes (1 mL HNO_3)	ICP – MS	Analytica AB	No limit
Radon and Radium isotopes	^{222}Rn, ^{226}Ra	Plastic	500	No	No	EDA, RD-200	IFE SUERC	Immediate transport
Dissolved gas (content and composition)	Ar, N_2, CO_2, O_2, CH_4, H_2, CO, C_2H_2, C_2H_4, C_2H_6, C_3H_8	Cylinder of stainless steel	200	No	No	GC	Paavo Ristola OY	Immediate transport
Colloids	Filter series and fractionation (see below)	Polycarbonate filter	0.45, 0.2 and 0.05 µm	-	N_2 atmosphere	ICP-AES ICP-MS	Analytica AB	Immediate transport
Humic and fulvic acids	Fractionation	Fractions are collected in plastic bottles	250	-	N_2 atmosphere	UV oxidation, IR (DOC)	Paavo Ristola OY	Immediate transport
Archive samples with acid	-	Plast (washed in acid)	100×2 **	Yes	Yes (1 mL HNO_3)	-	-	Storage in freeze container
Archive samples without acid	-	Plastic	250×2 **	Yes	No	-	-	Storage in freeze container

Component group	Component/ element	Sample container (material)	Volume (mL)	Filtering	Preparation/ Conservation*	Analysis method	Laboratory***	Analysis within - or delivery time to lab.
Carbon isotopes in humic and fulvic acids	∂^{13}C, pmC (^{14}C)	DEAE cellulose (anion exchanger)	-	-	-	(A)MS	The Ångström laboratory, Uppsala	A few days

* Suprapur acid is used for conservation of samples.

** Minimum number, the number of archive samples can vary depending on how many similar samples that are collected at the same occasion.

*** Full name and address is given in Table A2-3.

Abbreviations and definitions:

IC	Ion chromatograph
ISE	Ion selective electrode
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
MS	Mass Spectrometry
LSC	Liquid Scintillation Counting
(A)MS	(Accelerator) Mass Spectrometry
GC	Gas Chromatography

Table A7-2. Reporting limits and measurement uncertainties

Component	Method	Detection limit	Reporting limit or range	Unit	Measurement uncertainty[2]	"Total" uncertainty[3]
HCO_3	Alkalinity titration	0.2	1	mg/L	4 %	<10 %
Cl^- Cl^-	Mohr titration IC	5 0.2	70 0.5	mg/L	5 % 6 %	<10 % 10 %
SO_4	IC	0.2	0.5	mg/L	6 %	15 %
Br^- Br^-	IC ICP	0.2 -	0.7 0.001 – 0.010[1]	mg/L	9 % 15 %	20 %
F^- F^-	IC Potentiometry	0.2 -	0.6 -	mg/L	10 % -	20 % -
I^-	ICP	-	0.001 – 0.010[1]	mg/L	15 %	20 %
Na	ICP	-	0.1	mg/L	4 %	10 %
K	ICP	-	0.4	mg/L	6 %	15 %
Ca	ICP	-	0.1	mg/L	4 %	10 %
Mg	ICP	-	0.09	mg/L	4 %	10 %
S(tot)	ICP	-	0.160	mg/L	10 %	15 %
Si(tot)	ICP	-	0.03	mg/L	4 %	15 %
Sr	ICP	-	0.002	mg/L	4 %	15 %
Li	ICP	-	0.2 - 2[1]	µg/L	10 %	20 %
Fe	ICP	-	0.4-4[1]	µg/L	6 %	10 %
Mn	ICP	-	0.03-0.1[1]	µg/L	8 %	10 %
Fe (II), Fe(tot)	Spectrophotometry	5	20	µg/L	15 % (>30 µg/L)	20 %
HS^-	Spectrophotometry	0.02	0.03	mg/L	± 0.03 mg/L <0.2 mg/L	-
DOC	See tab. 1	-	0.5	mg/L	8 %	30 %
TOC	See tab. 1	-	0.5	mg/L	10 %	30 %
δ^2H	MS	-	2	‰ SMOW[4]	1.0 ‰	-

Component	**Method**	**Detection limit**	**Reporting limit or range**	**Unit**	**Measurement uncertainties**[2]	**”Total” uncertainties**[3]
$\delta^{18}O$	MS	-	0.1	‰ SMOW[4]	0.2 ‰	-
^{3}H	LSC	-	0.8 or 0.1	TU[5]	0.8 or 0.1 TU	-
$\delta^{37}Cl$	ICP MS	-	0.2 ‰ (20 mg/L)	‰ SMOC[6]	-	-
$\delta^{13}C$	A (MS)	-	>20 mg Carbon	‰ PDB[7]	-	-
pmC (^{14}C)	A (MS)	-	>20 mg Carbon	pmC[8]	-	-
δ^{34} S	ICP MS	-	0.2 ‰	‰ CDT[9]	0.2 ‰	-
$^{87}Sr/^{86}Sr$	MS	-	-	No unit (ratio)[10]	0.000020	-
$^{10}B/^{11}B$	ICP MS	-	-	No unit (ratio)[10]	0,0020	-
^{234}U, ^{235}U, ^{238}U, ^{232}Th, ^{230}Th	Alfa spectr.	-	0.05 (0.0005[13])	Bq/L[11]	0.05 Bq/L	Right order of magnitude
^{222}Rn, ^{226}Rn	LSC	-	0.1 (0.0005[13])	Bq/L	0.05 Bq/L	

[1] Reporting limits at salinity ≤ 0.4 % (520 mS/m) and ≤ 3.5 % (3810 mS/m) respectively.

[2] Measurement uncertainty reported by consulted laboratory, generally 95 % confidence interval.

[3] Estimated total uncertainty by experience (includes effects of sampling and sample handling).

[4] Per mille deviation[12] from SMOW (Standard Mean Oceanic Water).

[5] TU=Tritium Units, where one TU corresponds to a Tritium/hydrogen ratio of 10^{-18} (1 Bq/L Tritium = 8.45 TU).

[6] Per mille deviation[12] from SMOC (Standard Mean Oceanic Chloride).

[7] Per mille deviation[12] from PDB (the standard PeeDee Belemnite).

[8] The following relation is valid between pmC (percent modern carbon) and Carbon-14 age: $pmC = 100 \times e^{((1950-y-1.03t)/8274)}$
where y = the year of the C-14 measurement and t = C-14 age

[9] Per mille deviation[12] from CDT (the standard Canyon Diablo Troilite).

[10] Isotope ratio without unit.

[11] The following expressions are applicable to convert activity to concentration, for uranium-238 and thorium-232:
1 ppm U = 12.4 Bq/kg ^{238}U
1 ppm Th = 3.93 Bq/kg ^{232}Th

[12] Isotopes are often reported as per mill deviation from a standard. The deviation is calculated as:
$\delta^{y}I = 1000\times(K_{sample}-K_{standard})/K_{standard}$, where K= the isotope ratio and $^{y}I = {}^{2}H$, ^{18}O, ^{37}Cl, ^{13}C or ^{34}S etc.

[13] The consulted laboratory is changed recently and the new laboratory reports lower detection limits.

Table A7-3. Participant laboratories

Äspö water chemical laboratory (SKB) Mobile field laboratory, Forsmark (SKB)
Inainööritoimisto Paavo Ristola Oy Teollisuus-ja Voimalaitoskemia Rajantorpantie 8, C-talo 01600 Vantaa FINLAND
Dept. of System ecology Stockholm University 10691 Stockholm
Analytica AB Aurorum 10 977 75 Luleå (Nytorpsvägen 16 Box 511 183 25 Täby)
Environmental Isotope Laboratory Dep. Of earth sciences University of Waterloo Waterloo, Ontario N2L 3G1 CANADA
Institutt for energiteknik (IFE) Insituttveien 18 P.O Box 40 2027 Kjeller NORGE
AnalyCen Nordic AB Box 905 531 19 Lidköping
The Ångström laboratory Box 534 Se-751 21 Uppsala
Scottish Universities Environmental Research Centre (SUERC) Rankin Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland, UK.

Appendix 8

Compilation of water analysis data

Compilation June 2004

Table A8-1. Water Composition

Idcode	Secup m	Seclow m	Sample no.	Sampling date	Charge Bal %	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	HCO$_3^-$ mg/L	Cl$^-$ mg/L	SO$_4^{2-}$ mg/L	SO$_4$-S mg/L	Br mg/l	F$^-$ mg/L	Si mg/L	Fe mg/L	Fe-tot mg/L	FeII mg/L	Mn mg/L	Li mg/L	Sr mg/L
KFM04A	230,50	237,64	8154	2004-01-16	-1,4	1800	24,5	1340	212	96	5480	516	166	28	<0.2	5,2	5,04	3,47	3,47	2,58	0,056	13,7
KFM04A	230,50	237,64	8155	2004-01-20	-1,5	1810	24,8	1330	214	102	5490	521	166	27,6	<0.2	5,4	7,05	3,43	3,40	2,62	0,054	13,7
KFM04A	230,50	237,64	8156	2004-01-22	-1,7	1800	24,5	1330	218	102	5510	517	165	27,5	<0.2	5,4	7,13	3,46	3,43	2,61	0,057	13,6
KFM04A	230,50	237,64	8157	2004-02-04		-	-	-	-	111	-	-	-	-	-	-	-	-	-	-	-	-
KFM04A	230,50	237,64	8160	2004-02-05	-1,0	1810	26	1350	246	104	5550	511	167	27,8	<0.2	5,8	2,18	2,28	2,17	2,82	0,057	13,5
KFM04A	230,50	237,64	8267	2004-02-10	9,8	2820	25,6	1340	224	110	5580	514	167	29,5	<0.2	5,8	2,01	2,13	2,12	2,81	0,060	13,5
KFM04A	230,50	237,64	8269	2004-02-12	-3,7	1780	25,7	1300	224	112	5680	519	163	26,8	<0.2	5,9	1,98	2,16	1,08	2,78	0,055	13,4
KFM04A	354,00	361,13	8283	2004-04-20		-	-	-	-	79	5610	-	-	-	-	-	-	2,44	2,41	-	-	-
KFM04A	354,00	361,13	8285	2004-04-28		-	-	-	-	78	5620	-	-	-	-	-	-	2,34	2,35	-	-	-
KFM04A	354,00	361,13	8286	2005-05-04		1980	14,4	1540	166	79	5780	A	183	23,1	A	5,4	2,27	2,34	2,29	1,34	0,063	17,5
KFM04A	354,00	361,13	8287	2004-05-10		1980	13,8	1540	165	78	5780	A	181	22,6	A	5,4	2,13	2,10	2,16	1,31	0,054	17,5

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
ChargeBal % = Relative charge balance error %

SICADA: water_composition

Table A8-1. Water Composition

Idcode	Secup m	Seclow m	Sample no.	I^- mg/L	pH	DOC mg/L	TOC mg/L	HS^- mg/L	Drill_water %	ElCond mS/m	NH_4N mg/L
KFM04A	230,50	237,64	8154	-	7,28	8,8	-	0,02	11,5	1670	0,927
KFM04A	230,50	237,64	8155	-	7,25	A	-	0,01	10,6	1620	1,31
KFM04A	230,50	237,64	8156	-	7,29	1,9	-	0,02	10,7	1610	1,47
KFM04A	230,50	237,64	8157	-	7,31	-	-	-	7,6	1540	-
KFM04A	230,50	237,64	8160	-	7,28	A	-	<0.01	7,1	1630	0,648
KFM04A	230,50	237,64	8267	-	7,16	1,5	-	<0.01	7,5	1620	1,59
KFM04A	230,50	237,64	8269	-	7,20	1,4	-	<0.01	7,7	1610	1,60
KFM04A	354,00	361,13	8283	-	7,17	-	-	-	7,2	1660	-
KFM04A	354,00	361,13	8285	-	7,27	-	-	-	6,2	-	-
KFM04A	354,00	361,13	8286	0,049	7,32	A	-	A	6,5	1660	A
KFM04A	354,00	361,13	8287	0,048	7,27	A	A	A	6,5	1660	A

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
ChargeBal % = Relative charge balance error %

SICADA: water_composition

Table A8-2. Isotopes I (H-, O-, B-, S-, Cl- and C-isotopes)

Idcode	Secup m	Seclow m	Sample no.	Sampling date	δ^2H dev SMOW	^{3}H TU	δ^{18}O dev SMOW	^{10}B/^{11}B no unit	δ^{34}S dev CDT	δ^{13}C dev PDB	^{87}Sr/^{86}Sr no unit	^{14}C pmC	AGE_BP years	δ^{37}Cl dev SMOC
KFM04A	230,50	237,64	8154	2004-01-16	-70,9	1,0	-9,0	A	-	-	-	-	-	-
KFM04A	230,50	237,64	8155	2004-01-20	-70,4	<0.8	-9,6	A	-	-	-	-	-	-
KFM04A	230,50	237,64	8156	2004-01-22	-70,7	<0.8	-9,0	A	A	-	A	-	-	-
KFM04A	230,50	237,64	8160	2004-02-05	-70,6	<0.8	-9,1	A	-	-	-	-	-	-
KFM04A	230,50	237,64	8267	2004-02-10	-84,4	<0.8	-9,0	A	A	-	A	-	-	-
KFM04A	230,50	237,64	8269	2004-02-12	-68,3	<0.8	-9,1	A	-	-	-	-	-	-
KFM04A	354,00	361,13	8283	2004-04-20	A	A	A	A	-	-	-	-	-	-
KFM04A	354,00	361,13	8285	2004-04-28	A	A	A	A	-	-	-	-	-	-
KFM04A	354,00	361,13	8286	2005-05-04	A	A	A	A	A	-	A	-	-	-
KFM04A	354,00	361,13	8287	2004-05-10	A	A	A	A	A	A	A	A	A	A

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
SICADA: h_o_isotopes, b_s_cl_sr_isotopes, c_s_isotopes

Table A8-3. Trace elements

Idcode	Secup m	Seclow m	Sample no.	Sampling date	U µg/L	Th µg/L	Sc µg/L	Y µg/L	Zr µg/L	In µg/L	Sb µg/L	Cs µg/L	La µg/L	Hf µg/L	Tl µg/L	Ce µg/L	Pr µg/L	Nd µg/L	Sm µg/L
KFM04A	230,50	237,64	8156	2004-01-22	34,70	<0.2	<0.5	0,167	0,71	A	0,294	1,61	<0.05	<0.05	<0.03	<0.05	<0.05	<0.05	<0.05
KFM04A	230,50	237,64	8267	2004-02-10	62,00	<0.2	<0.5	0,42	0,315	A	0,278	1,76	<0.05	<0.05	<0.03	<0.05	<0.05	<0.05	<0.05

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
SICADA: trace_elements

Table A8-3. Trace elements

Idcode	Secup m	Seclow m	Sample no.	Eu µg/L	Gd µg/L	Tb µg/L	Dy µg/L	Ho µg/L	Er µg/L	Tm µg/L	Yb µg/L	Lu µg/L
KFM04A	230,50	237,64	8156	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
KFM04A	230,50	237,64	8267	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

- = Not analysed
A = results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
SICADA: trace_elements

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Table A8-4. Isotopes II (U-, Th, Ra- and Rn-isotopes)

Idcode	Secup m	Seclow m	Sample no.	Sampling date	^{238}U mBq/L	^{235}U mBq/L	^{234}U mBq/L	^{232}Th mBq/L	^{230}Th mBq/L	^{226}Ra Bq/L	^{222}Rn Bq/L
KFM04A	354,00	361,13	8287	2004-05-10	A	A	A	A	A	1,32	110

- = Not analysed
A = Results will be reported later
x = No result due to sampling problems
xx = No result due to analytical problems
< "value" = result below detection limit
SICADA: u_th_isotope_t, ra_rn_isotope_t