

Oskarshamn site investigation

Hydrochemical logging in KSH03A

Results from isotope determinations (³H, δD, δ¹⁸O and δ³⁷Cl)

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March 2005

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Keywords: Core drilled borehole, Groundwater, Water sampling, Chemical analyses, Isotope determinations.

This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author and do not necessarily coincide with those of the client.

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Abstract

Hydrochemical logging or, so called tube sampling, has been performed in the core drilled borehole KSH03A. The method is a fast and simple sampling technique for obtaining information of the chemical composition of the water column along an open borehole. The equipment consists of an approximately 1,000 metres long polyamide tube divided into units of 50 metres.

The water content in each tube unit constituted one sample. Every second sample, starting with the uppermost unit, was analysed according to SKB chemistry class 3 (options excluded). The performance of the hydrochemical logging in KSH03A and the results from the analysis mentioned above has been reported in a previous report /1/. The following report gives the results from the performed isotope determinations of tritium (^3H), deuterium (δD), $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$. Samples for isotope determinations were collected at the sampling occasion and stored in a freezer for approximately two months before they were sent to the consulted laboratories for analyses. Odd numbered tube units were analysed for $\delta^{18}\text{O}$ and deuterium while even numbered tube units were analysed for tritium and $\delta^{37}\text{Cl}$.

Sammanfattning

Hydrokemisk loggning, även kallad slangprovtagning, har utförts i kärnborrhålet KSH03A. Hydrokemisk loggning är en snabb och enkel provtagningsteknik för att erhålla information om vattenpelarens kemiska sammansättning längs ett öppet borrhål. Utrustningen utgörs av en cirka 1 000 meter lång polyamid slang uppdelad i enheter om vardera 50 meter.

Innehållet i en slangenhet utgör ett prov. Varannan enhet, med start från den översta, analyserades i enlighet med SKB kemiklass 3 utan tillägg i direkt anslutning till provtagningstillfället. Utförande och resultat från dessa analyser har rapporterats i en tidigare primärdatarapport /1/. Denna rapport redovisar resultaten från utförda isotopanalyser av tritium (^3H), deuterium (δD), $\delta^{18}\text{O}$ och $\delta^{37}\text{Cl}$. Isotopprover togs ut i samband med provtagningen och sparades i frys i cirka två månader innan de sändes iväg för analys till de konsulterande laboratorerna. Udda slangenheter, räknat från den översta enheten, analyserades med avseende på $\delta^{18}\text{O}$ och deuterium medan jämna enheter analyserades för tritium och $\delta^{37}\text{Cl}$.

Contents

1	Introduction	7
2	Objective and scope	9
3	Performance	11
3.1	Hydrochemical logging	11
3.2	Sample treatment and chemical analysis	11
3.3	Data handling	13
3.4	Nonconformities	14
4	Results	15
4.1	Analysis results	15
4.2	Quality of the analyses	16
5	References	17
	Appendix 1 Sampling and analysis methods	19
	Appendix 2 Isotopes, compilation of H-, O- and Cl-isotopes	21

1 Introduction

This document reports isotope results from the Hydrochemical logging in KSH03A, which is one of the activities performed within the site investigation at Oskarshamn /2/. The work was carried out in accordance with activity plan SKB PS 400-03-059. In Table 1-1 controlling documents for performing this activity are listed. Both activity plan and method descriptions are SKB's internal controlling documents.

This report is a complement to the previous report regarding Hydrochemical logging in KSH03A /1/, which documented the performance and results from analyses of major components, anions, flushing water content, electric conductivity, pH and hydrogen carbonate. The data from the activity is reported to SICADA.

Table 1-1. Controlling documents for the performance of the activity.

Activity plan	Number	Version
Hydrokemisk loggning i KSH03	AP PS 400-03-059	1.0

Method descriptions	Number	Version
Metodbeskrivning för hydrokemisk loggning	SKB MD 422.001	1.0

2 Objective and scope

Hydrochemical logging was performed in order to obtain an overview of the chemical composition of the water along the open borehole KSH03A. The technique used for sampling is fast and simple even at great depth.

The analysis program has previous been carried out according to SKB chemistry class 3 (excluding options) and has been reported in a previous report /1/. The isotopes reported in this report were sent to be analysed approximately two months after the sampling occasion i.e. in the end of March. Until they were sent for analyses they were stored in a freezer. The conducted isotope determinations include tritium, deuterium, $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$.

3 Performance

3.1 Hydrochemical logging

The hydrochemical logging in KSH03A was performed January 27, 2004, according to the activity plan and following the method description.

The performance of the activity is described in a previous report regarding the hydrochemical logging in KSH03A /1/.

3.2 Sample treatment and chemical analysis

An overview of sample treatment and analysis routines is given in Appendix 1.

An overview showing the samples obtained at the logging occasion is given in Table 3-1. The sample portions for isotope analyses were stored in freezer at SKB at the time of the hydrochemical logging. Samples collected for determination of tritium, $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$ and deuterium were analysed at the consulted laboratories approximately two months after the sampling performance. Remaining collected isotope samples are still stored in a freezer. The data from the hydrochemical logging are stored in the SICADA database. The SKB sample numbers are 7086 to 7105.

Table 3-1. Overview of samples collected at the hydrochemical logging in KSH03A. Filled cells represent collected samples. Light yellow filling represents isotope samples that has been analysed, blue filling represents analysed samples reported in a previous report /1/, dashed yellow filling represents samples stored in a freezer and purple dashed cells represents archive samples.

Sample information			Collected sample portions									Archive
Tube unit	Length (m)	SKB no.	Cond., pH, alk.	Major Comp.	Uranine	An-ions	$\delta^{34}\text{S}$	$\delta\text{D} / \delta^{18}\text{O}$	^{87}Sr	$^3\text{H} / \delta^{37}\text{Cl}$	Carbon isotopes	Filtered 2x250 mL
1	0-40	7086		Relative charge balance error			ω	ω	ω			
2	90	7087										
3	140	7088		Relative charge balance error								
4	190	7089										
5	240	7090										
6	290	7091										
7	340	7092										
8	390	7093										
9	440	7094										
10	490	7095										
11	540	7096										
12	590	7097										
13	640	7098										
14	690	7099										
15	740	7100										
16	790	7101										
17	840	7102										
18	890	7103										
19	940	7104										
20	990	7105										

ω filled with sample water from tube unit two.

ω partly filled with sample water from tube unit two.

The upper most tube unit was not completely filled, see section 3.1. Due to the lack of water in the first tube unit, archive samples from the second tube unit could not be filled. Water intended for archive samples in the second unit were used to fill sample bottles for δD and $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ from the first section (0–40 m).

3.3 Data handling

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

All analytical results were 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 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:

- Calculation of charge balance errors. Relative errors within $\pm 5\%$ are considered acceptable.

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

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

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 3-1.

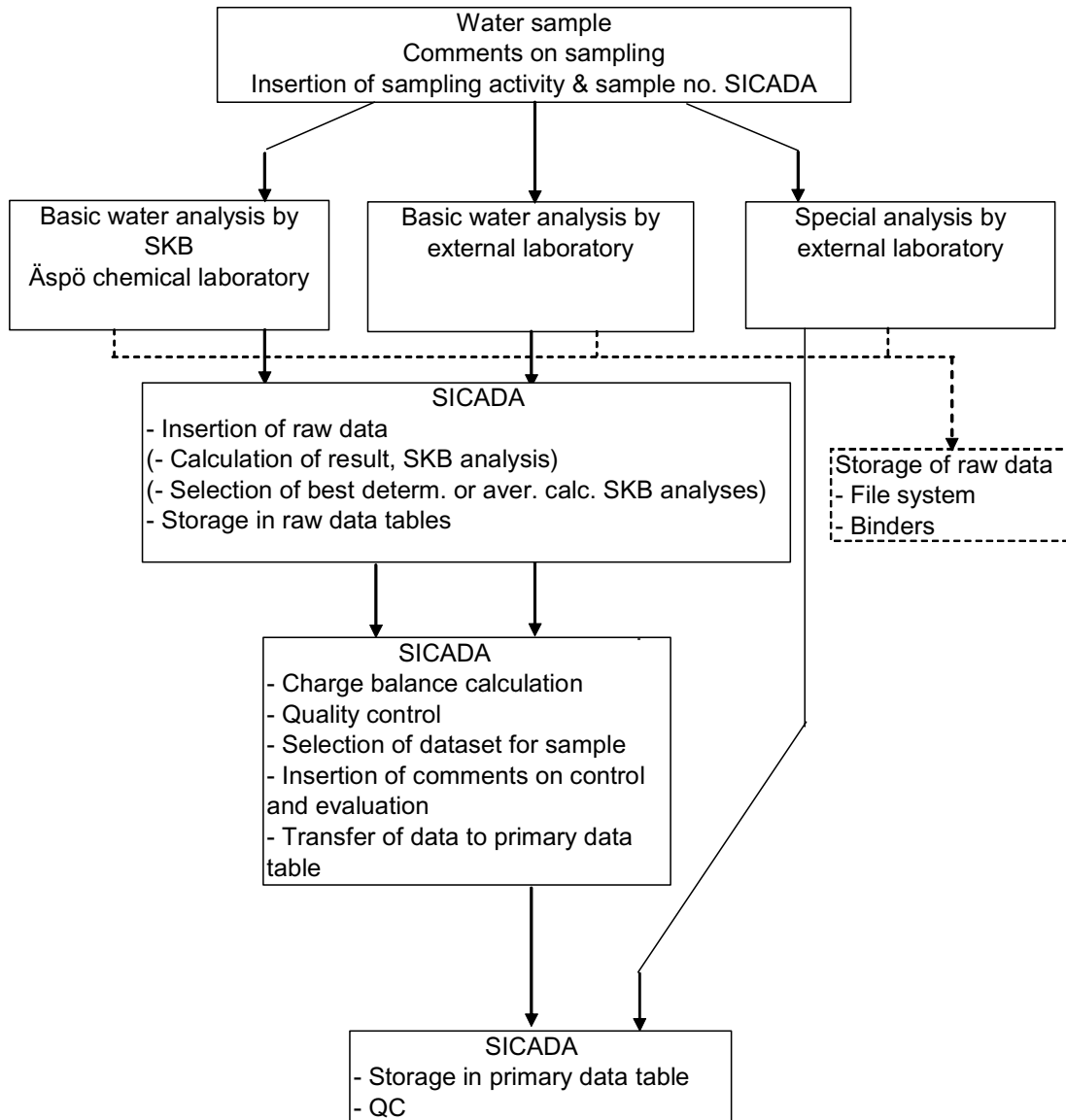


Figure 3-1. Overview of data management for hydrogeochemical data. This report handles only the “Special analysis by external laboratory”. (The basic water analyses are reported in the previous report /1/).

3.4 Nonconformities

The activity was performed without any deviations from the controlling documents listen in Table 1-1.

4 Results

4.1 Analysis results

The results from the conducted isotope determinations are given in Appendix 2. Diagrams showing the tritium and $\delta^{18}\text{O}$ values along the borehole received from the hydrochemical logging are presented in Figure 4-1. Results from deuterium determinations are shown in Table 4-1. Results are plotted for the mid-length of each tube unit.

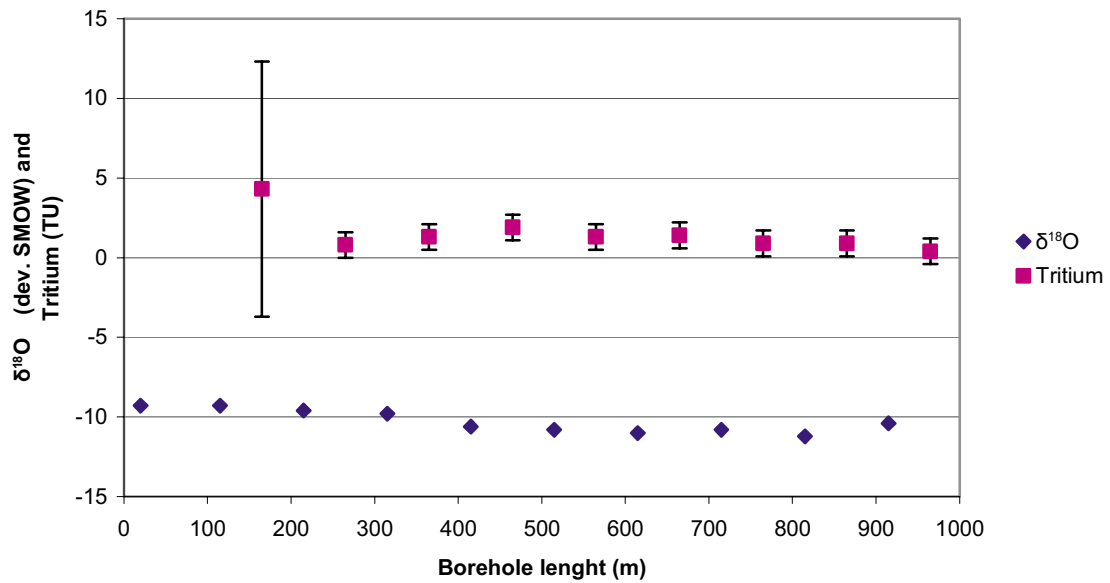


Figure 4-1. Tritium and $\delta^{18}\text{O}$ data from samples collected in the core drilled borehole KSH03A at the hydrochemical logging. The first sample was run as direct tritium while the other eight were run as enriched tritium.

Table 4-1. δD and $\delta^{37}Cl$ determinations for samples collected at the hydrochemical logging in KSH03A.

Sample SKB:no	δD (dev. SMOW)	$\delta^{37}Cl$ (dev. SMOC)
7086	-70.4	
7087		-0.07
7088	-55.1	
7089		-0.09
7090	-69.9	
7091		-0.02
7092	-73.4	
7093		0.18
7094	-75.5	
7095		0.39
7096	-75.9	
7097		0.28
7098	-76.7	
7099		0.33
7100	-76.7	
7101		0.39
7102	-76.2	
7103		0.29
7104	-68.0	
7105		0.81

4.2 Quality of the analyses

Direct and enriched analyses differ when the samples are below 30 TU (tritium units). The enrichment system concentrates tritium so the precision count below 1 DPM (disintegrations per minute) improves. A sample run as direct tritium has a precision of ± 8 TU while a sample run as enriched tritium has a precision of ± 0.8 TU. In contrast to a direct sample an enriched sample is electrolysed from 250 mL to 15 mL, i.e. the H_2O molecule is cracked with an electrical current into hydrogen and oxygen keeping the HTO (tritiated/heavy water) intact, before analysis.

Sample number 7087 had an organic smell and was foamy which enabled the consulted laboratory to perform the determination of tritium in the sample. It was considered inadvisable to run both as enriched and as direct tritium.

The smell and foam was also noticed for sample number 7089, but not to the extent as in the sample mentioned above. Due to the nature of the sample it was considered preferable to run as direct tritium instead of enriched tritium. The origin of the smell and foam in the samples is not known.

At the sampling occasion the two samples above had some unidentified yellow precipitation in them, which may be the cause of the smell and/or foam.

5 References

- /1/ **Berg C, 2004.** Oskarshamn site investigation. Hydrochemical logging in KSH03A. SKB P-04-51, Svensk Kärnbränslehantering AB.
- /2/ **SKB, 2001.** Generellt genomförande program för platsundersökningar. SKB R-01-10, Svensk Kärnbränslehantering AB.

Sampling and analysis methods

Table A1-1. Overview of general 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	Äspö's chemistry lab.	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 ⁻ , SO ₄ , Br ⁻ , F ⁻) ISE (F ⁻)	Äspö's chemistry lab.	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	Not critical (month)
Environmental isotopes	² H, ¹⁸ O	Plastic	100	No	–	MS	IFE	Not critical (month)
Tritium, Chlorine-37	³ H (enhanced) Chlorine-37	Plastic (dry bottle) Plastic	500 100	No No	– –	LSC ICP MS	Univ. of Waterloo	Not critical (month)
Carbon isotopes	¹³ C, ¹⁴ C	Glass (brown)	100×2	No	–	(A)MS	Univ. of Waterloo The Ångström laboratory, Uppsala	A few days
Sulphur isotopes	³⁴ S	Plastic	500–1,000	Yes	–	Combustion, ICP MS	IFE	No limit
Strontium-isotopes	⁸⁷ Sr/ ⁸⁶ Sr	Plastic	100	Yes	–	TIMS	IFE	Days or Week
Boron isotopes	¹⁰ B	Plastic	100	Yes	Yes (1 mL HNO ₃)	ICP-MS	Analytica AB	No limit
Archive samples without acid	–	Plastic	250×2**	Yes	No	–	–	Storage in freeze

* 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 A1-2.

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 A1-2. Consulted laboratories, full name and address.

Äspö waterchemical laboratory (SKB)

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

The Ångström laboratory
Box 534
Se-751 21 Uppsala

Appendix 2

Isotopes, compilation of H-, O- and Cl-isotopes

Compilation March 2005

Idcode	Secup m	Seclow m	Sample no	δD dev SMOW	3H TU	$\delta^{18}O$ dev SMOW	$\delta^{37}Cl$ dev SMOC	$^{10}B/^{11}B$ no unit	$^{87}Sr/^{86}Sr$ no unit	$\delta^{34}S$ dev CDT	$\delta^{13}C$ dev PDB	^{14}C pmC
KSH03A	0	40	7086	-70.4	-	-9.3	-	xxx	xxx	xxx	-	-
KSH03A	40	90	7087	-	xx	-	-0.07	-	-	-	xxx	xxx
KSH03A	90	140	7088	-55.1	-	-9.3	-	xxx	xxx	xxx	-	-
KSH03A	140	190	7089	-	4.3*	-	-0.09	-	-	-	xxx	xxx
KSH03A	190	240	7090	-69.9	-	-9.6	-	xxx	xxx	xxx	-	-
KSH03A	240	290	7091	-	0.8	-	-0.02	-	-	-	xxx	xxx
KSH03A	290	340	7092	-73.4	-	-9.8	-	xxx	xxx	xxx	-	-
KSH03A	340	390	7093	-	1.3	-	0.18	-	-	-	xxx	xxx
KSH03A	390	440	7094	-75.5	-	-10.6	-	xxx	xxx	xxx	-	-
KSH03A	440	490	7095	-	1.9	-	0.39	-	-	-	xxx	xxx
KSH03A	490	540	7096	-75.9	-	-10.8	-	xxx	xxx	xxx	-	-
KSH03A	540	590	7097	-	1.3	-	0.28	-	-	-	xxx	xxx
KSH03A	590	640	7098	-76.7	-	-11.0	-	xxx	xxx	xxx	-	-
KSH03A	640	690	7099	-	1.4	-	0.33	-	-	-	xxx	xxx
KSH03A	690	740	7100	-76.7	-	-10.8	-	xxx	xxx	xxx	-	-
KSH03A	740	790	7101	-	0.9	-	0.39	-	-	-	xxx	xxx
KSH03A	790	840	7102	-76.2	-	-11.2	-	xxx	xxx	xxx	-	-
KSH03A	840	890	7103	-	0.9	-	0.29	-	-	-	xxx	xxx
KSH03A	890	940	7104	-68.0	-	-10.4	-	xxx	xxx	xxx	-	-
KSH03A	940	990	7105	-	<0.8	-	0.81	-	-	-	xxx	xxx

- = Not analysed.

A = Results will be reported later.

x = No result due to sampling problems.

xx = No result due to analytical problems.

xxx = Stored in a freezer.

* = Analysed as direct tritium.

< = Result below detection limit.