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Äspö Hard Rock Laboratory

TRUE Block Scale Project
Detailed characterisation stage

Test of New possible non-reactive tracers
Experimental description and evaluation

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

Abstract

This report describes a series of pilot tracer tests performed at Äspö HRL with the purpose of identifying 5-10 new non-reactive tracers. These tracers should be used in the forthcoming tracer tests performed within the TRUE Block Scale Project. The relatively large distances and the complex flow geometry expected will most certainly induce a large dilution of the tracers along the flow paths and in the sink section. It was therefore essential to identify tracers with a large dynamic range (relation between solubility and detection limit).

Sammanfattning

Denna rapport beskriver en pilotstudie av spårförsök utförda i Äspö HRL i syfte att identifiera 5-10 nya icke-reaktiva spårämnen. Dessa spårämnen skall användas i de kommande spårförsöken inom TRUE Block Scale projektet. De relativt långa avstånden och de komplexa flödesgeometrier som förväntas kommer högst sannolikt att medföra stor utspädning av spårämnena längs flödesvägarna och i uttagssektionen. Det var därför viktigt att kunna identifiera spårämnen med ett stort dynamiskt mätområde (förhållande mellan löslighet och detektionsgräns).

Executive Summary

A series of tracer experiments within the ongoing TRUE Block Scale Project will be performed over distances between 10-50 metres and in a network of structures. The large distances and the complex flow geometry will most certainly induce a large dilution of the tracers along the flow path and in the sink section. These tests will require 5-10 non-reactive tracers that can be detected in very low concentrations.

The aim of this study was to identify at least five new non-reactive tracers to be used in the planned tracer tests within the TRUE Block Scale Project. Apart from the obvious demand of non-reactiveness, the evaluation of the tracers also included the price and the availability of the tracer and of the analysis in question. Another criterion of the analysis has been the demand for high accuracy and detectability.

This study was performed by injecting a total of 23 different tracers in radially converging flow geometry over a distance of about 3-m within Feature B at the TRUE-1 site, Äspö HRL. The study was divided in to two separate test runs. The non-reactive tracer Uranine was used as reference in both tests. The first pilot test run included the fluorescent dye tracer Phloxine and seven metal-complexes (Ho-DTPA, Gd-DTPA, Yb-EDTA, Lu-EDTA, In-EDTA, Ni-EDTA and ReO_4). The second pilot test run included three injections with a mixture of dyes (Uranine, Eosin, Dimethylfluorescein, Sulforhodamine G, Naphtionate, Pyranine, UV-1), deuterium, helium, and the dye tracer Rose Bengal accompanied by five fluorinated benzoic acids (2,3-DFBA, 2,6-DFBA, 3,5-DFBA, 2,3,4,5-TFBA and 2,3,4,5, 6-PFBA). The analysis methods were fluorometry and HPLC for the fluorescent dyes, ICP-MS for the metal-complexes and LC-MS-MS for the analysis of the fluorinated benzoic acids.

Breakthrough from all the injected tracers in the first pilot test was detected in the pumping section. Breakthrough curves for the new tracers were compared to the curve of Uranine. Due to the few analyses of the metal-complexes made in the injection loop the mass recovery was calculated under the assumption that the same relative mass for the metal-complexes is injected as for Uranine. The mass recovery of Uranine was calculated (and measured) to 100%, the majority of the metal-complexes had slightly lower mass recoveries, 81-93%. ReO_4 had a very high mass recovery, 110%, which may be explained by analysis errors. Phloxine, Rose Bengal and Ni-EDTA suffered irreversible losses and had mass recoveries less than 50%.

The results from the second test run indicated that Helium is possible to use in future tests and also that it may be possible to distinguish diffusion effects by comparison with other tracers. Of the dyes tested, Eosin, Dimethylfluorescein, Naphtionate, Pyranine and UV-1, seem to be non-reactive whereas Sulforhodamine G and Rose Bengal are sorbed. The analysis of the fluorinated benzoates could only be made after development of a new method of analysis taht allowed detection levels down to a factor 100 lower than previously possible in commercial laboratories. The test showed mass losses of all benzoic acids compared to Uranine, but no obvious delay or excessive tailing of the breakthrough curve indicating reactive processes. The long time of storage of the water samples (>1 year) may have resulted in mass losses due to e.g. microbial degradation.

Contents

1 Introduction

1.1 Background

A series of tracer experiments will be performed within the ongoing TRUE Block Scale Project. The experiments will be performed over distances between 10-50 m in a network of structures. The long distances and complex flow geometry will most probably induce a large dilution of the tracers along the flow path and in the sink section. It is envisaged that these tests require between 5-10 non-reactive tracers that can be detected in very low concentrations.

Tracer experiments have also been performed within the TRUE-1 Project at Äspö HRL (Winberg et al., 2000). These tests were performed over distances between 2.5 to 10 meters in a single fracture. In total 11 different non-reactive tracers have been used in TRUE-1 tests, cf. Table 1-1. However, some of them were found to be weakly sorbing, others suffered irreversible mass losses, and some of them were radioactive. The latter group (HTO, ^{82}Br, ^{131}I) will probably not be possible to use other than in a very controlled experiment were mass losses are unlikely to occur.

This report describes the results and preliminary evaluation of the investigation of new possible non-reactive tracers for Äspö conditions. Some of the tracers have been used earlier at other sites or in other rock types than present at Äspö, while some are more or less untested in the field.

1.2 Objectives

The objective of this study is to identify at least five new non-reactive groundwater tracers that may be used in the planned tracer tests within the TRUE Block Scale Project. The tracers may not necessarily have to new with regards to their use as groundwater tracers, but the application of the tracers in the Äspö HRL environment will be new.

Table 1-1: Non-reactive tracers used in the TRUE-1 experiments.

Tracer	Type	Test	Comment
Uranine	Fluorescent dye	All	Reference tracer
Amino G Acid	Fluorescent dye	RC-1, DP-2,4,5 PDT-1,2	Good but high background and not available any more
Rhodamine WT	Fluorescent dye	RC-1	Weakly sorbing
Eosin Y	Fluorescent dye	RC-1	Solubility problems, less dynamic range
Gd-DTPA	Metal-complex	RC-1, DP-1	Irreversible losses, expensive analysis
Eu-DTPA	Metal-complex	RC-1	Irreversible losses, expensive analysis
Ho-DTPA	Metal-complex	RC-1	Irreversible losses, expensive analysis
Tb-DTPA	Metal-complex	RC-1	Irreversible losses, expensive analysis
HTO	Tritiated water	PDT-3, STT-1 STT-1b, STT-2	Good but restrictions may be necessary
^{82}Br	Radioisotope	PDT-3, STT-1b, STT-2	Good but restrictions may be necessary
^{131}I	Radioisotope	STT-1b	Good but restrictions may be necessary

2 Literature study of ground water tracers

2.1 Basis for the study

The objective of the literature study was to identify possible new non-reactive ground water tracers to be used in the tracer tests. The study was focused on the possible new tracers presented in Table 2-1. The basis for Table 2-1 is a compilation of tracer tests in fractured media by Andersson (1995) and a doctoral thesis by Byegård (1995).

Table 2-1: Non-reactive tracers to be studied in the literature study.

Tracer	Name	Analysis	Dynamic Range	Comment
Gases	He-3	Mass spectrometry	Large	Used by NAGRA
	Ar, Ne, Xe		?	Research needed
Stable isotopes	Deuterium	Mass spectrometry	?	Expensive analysis
	N-15, C-13, 0-18		?	
Dyes	Eosin B, Y	Fluorometry	Large	Used in TRUE-1
	Phloxine			Used in Stripa
	Rose Bengal			Used in Stripa
	MTMBA			SOLEXPERTS
	UV-1			Hydroisotop
Metal-Complexes	m-EDTA	ICP-MS	Large	Used in Finnsjön, Stripa, TRUE-1
	m-DTPA			
	m-DOTA			
Halogenated hydrocarbons	Many different	Gas chromatography	Large	Used in USA, Hydroisotop has experience. Possible environmental constraints
Benzoates	TFMBA and others	HPLC	Large?	Used by SANDIA in USA
Particles		Particle counter	?	Study at CTH Nuclear Chemistry
Others	ReO_4	ICP-MS	Large	Used in Finnsjön
	CS_2	?	?	

2.1.1 General

One of the many aspects that makes the task of identifying new possible non-reactive ground water tracers to be used at Äspö HRL a difficult one is the fact that there are not many tracer tests performed in crystalline rock. An overwhelming majority of the tracer tests in the literature are performed in sediments or in sedimentary rock.

Another difficulty of finding new possible non-reactive ground water tracers suitable for use at Äspö HRL lies in the fact that most tracer tests in the literature are made with the same set of tracers. One reason for this may be the fact that most tracer tests mentioned in the literature does not require more than only a few tracers. This makes the choice of using well-known and well-documented non-reactive tracers a natural one.

Compounds to be considered possible new non-reactive ground water tracers must fulfil the following requirements (Stetzenbach and Farnham; 1994):

1) Must be water soluble

2) Should not sorb to aquifer material

3) Should be chemically and biologically stabile for the duration of the test

4) Should be foreign to the test

5) Should be non-toxic

6) Should have excellent analytical sensitivity

The planned tests at Äspö HRL, involving large distances and high salinity of the water will also require tracers that have a large dynamic range. The dynamic range is defined as the span between solubility and lowest detection limit.

2.1.2 Gases

He has been used as non-reactive groundwater tracer in Grimsel (Frick et al., 1992) with good results. The advantage of using He is that the diffusivity of He is significantly higher than for other tracers. Thus, the possibility of identifying matrix diffusion increases by using He.

^{3}He was chosen as noble gas tracer in both pilot tests due to its low background concentration in the formation water, which is below the detection limit of the used He detection device.

Compared to ^{4}He equilibration concentration of air exposed surface waters, natural ground waters exhibit much higher ^{4}He levels. This is especially pronounced in subsurface waters coming into contact with U-rich rocks. The very large increase of ^{4}He concentration in subsurface waters compared to sea or rain water results from additional in-situ underground ^{4}He production via decay of U, Th and their daughter isotopes. These reactions may be summarised as:

$$^{238}U \rightarrow {}^{206}Pb + 8\ {}^{4}He$$
$$^{235}U \rightarrow {}^{207}Pb + 7\ {}^{4}He$$
$$^{232}Th \rightarrow {}^{208}Pb + 6\ {}^{4}He$$

Since major parts of crustal uranium is sited in fine grained disseminations on the surfaces of rock forming minerals (Rich et al., 1977), circulating pore water readily picks up ^{4}He by direct contact recoil or during alteration of uranium minerals. Surface-exposed waters contain a low ^{4}He concentration of about 10^{-8} ccSTP/ml (Ozima and Podosek, 1983), which corresponds to a leak rate of about 10^{-9} mbarliter/sec. The ^{4}He

leak rate measured in the test site ground water (free outflow out of KXTT4:R4) was 7.2 10^{-6} mbarliter/sec. After 5 min of free outflow, the leak rate signal was stable. No gas bubbles caused by degassing were observed, which could have biased the He detection. The measured leak rate value corresponds to a ^{4}He concentration on the order of 10^{-6} to 10^{-5} ccSTP/ml. The 100 to 1000 times higher ^{4}He concentration compared to surface water originates most likely from in-situ underground production. In the groundwater of the migration fracture at the Grimsel Test Site (grano-diorite), which has a relatively short residence time in the Grimsel rock of 30 – 50 years (Frick et al. 1992), a similar ^{4}He concentration was measured 3-4 10^{-6} ccSTP/ml (Eikenberg et al, 1992).

Other possible noble gases are Ar, Ne and Xe. However, currently no simple method of analysis as the in-line detection method for He exists.

2.1.3 Stable isotopes

Deuterated water is an ideal tracer for the determination of water movement. It shows no absorption or retardation. In comparison with the other tracers, Deuterated water can have an exchange with the stationary water. Deuterated water was therefore chosen for the pilot tests. Other stable isotopes like ^{15}N, ^{13}C and ^{18}0 were not considered due to the high costs.

2.1.4 Fluorescent dyes

Fluorescent dyes are probably the most frequently used type of tracer. They are easy to handle, to detect and prices are generally low. Fluorescent dyes are in general non-toxic. Concentrated dyes should however be treated with care. Fluorescent dyes can with HPLC and spectrofluorometry be readily analysed at $\mu g\ L^{-1}$ levels. A cocktail of fluorescent dyes can be used simultaneously if the dyes are chosen so that they do not interfere analytically with each other. The best distinction with HPLC is given if the dyes of interest appear at different times in the chromatogram. If dyes with overlapping spectra are retarded differently on the chromatographic column the spectral overlap does not interfere, because the dyes appear at different times at the detector. The distinction of dyes using spectrofluorometry is a question of spectral distance but also of differences in excitation spectra of the dyes in question. If the differentiation of tracers is based only on differences in wavelength, then the difference between excitation maxima should be at least 25 nm. Excitation variations due to variations in pH can be used to distinguish between two dyes that exhibit fluorescence at the same wavelength. Dyes that disturb the analysis of other dyes can de destroyed by selective oxidation. The use of these and other methods with optimal use of the spectral characteristics is understood as ‘advanced spectrofluorometric techniques’. A thorough investigation including eight of the most commonly used dyes was made by Smart and Laidlaw (1977). Three of the investigated dyes, Uranine, Amino G Acid and Rhodamine WT been used in the TRUE Project (Andersson 1996) and are known to be non-reactive. Phloxine B and Rose Bengal (Abelin et. al 1987; Käss, 1998) are mentioned in the literature and show qualities that makes them candidates for the pilot tests.

The dyes chosen for the pilot tracer tests were selected according to their expected transport behaviour as well as the possibility of their individual detection in the tracer cocktail. Price and toxicity was also weighed into the selection process. Data of the dyes are given in Table 2-2.

Table 2-2: Fluorescent tracer selected for the pilot tracer tests (including alternative names).

Tracer	CAS-No	Sum formula	C.I. No	Generic name	Excitation max (nm)	Emission max (nm)
Uranine						
	[518-47-8]	$C_{20}H_{10}Na_2O_5$	45350	Acid Yellow 73	492	515
	Disodium salt of 2-(6-hydroxy-3-oxo-3H-xanthene-9-yl)-benzoic acid; Disodium-fluorescein					
Eosin Y						
	[17372]	$C_{20}H_6O_5Na_2Br_4$	45380	Acid Red 87	513	530
	Disodium salt of 2´,4´,5´,7´-tetrabromo-fluorescein; Disodium salt of 2-(6-hydroxy-3-oxo-2,4,5,7-tetrabromo-3*H*-xanthene-9-yl)-Benzoic acid					
Sulforhodamine G						
	[5873-16-5]	$C_{28}H_{33}N_2NaO_7S_2$	45220	Acid Red 50	532	555
	Sodium salt of 4-(3,6-bis-ethylamino-2,7-dimethyl-3*H*-xanthene-9-yl)-(benzene-1,3-disulfonic acid)					
Pyranine						
	[59040]	$C_{16}H_7Na_3O_{10}S_3$	59040	Solvent Green 7	03/458	513
	Trisodium salt of 8-hydroxy-1,3,6-pyrenetrisulfonic acid					
Dimethylfluorescein						
		$C_{22}H_{14}Na_2O_5$			495	519
	Disodium salt of 2-(6-hydroxy-3-oxo-5,7,dimethyl-3*H*-xanthene-9-yl)-benzoic acid; Disodium-dimethylfluorescein					
Naphthionate						
	[130-13-2]	$C_{10}H_8Na_3O_3S$	(no colour)		330	420
	Sodium salt of 4-amino-naphthalene-1-sulfonic acid					
Phloxine B						
	[18472-87-2]	$C_{20}H_2Br_4Cl_4Na_2O_5$	45410	Acid Red 92	510	548
Rose Bengal						
	[632-69-9]	$C_{20}H_2Cl_4I_4Na_2O_5$	45440	Acid Red 94	510	548
UV1						
	special tracer created by Mr. Behrens, Hydroisotop					

2.1.5 Metal-complexes

Metal-complexes have earlier been used in several investigations for SKB in Finnsjön (Gustafsson and Nordqvist, 1993; Andersson et. al, 1993) and Stripa (Olsson (*ed)*, 1992). The Stripa investigations included injections of five DTPA-complexes (Dy, Eu, Gd, Ho and Tb) and perrhenat (ReO_4^-), each one combined with a dye tracer. The results indicated that the DTPA-complexes and perrhenat were less reactive than the dyes, including Uranine. The investigations in Finnsjön included a number of radioactive metal-complexes and six non radioactive EDTA-complexes (In, Dy, Ho, Er, Tm and Yb), Gd-DTPA and perrhenat. All tracers were combined with a dye tracer. The result from Finnsjön indicated that some of the complexes are well suited as non-reactive ground water tracers while others suffered irreversible losses or sorbed.

Metal-complexes can be analysed at hundredths of $\mu g\ L^{-1}$ levels using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). The cost and availability of the tracer itself and the detection method of choice are important aspects when deciding on a tracer. The metal-complexes have to be specially manufactured and the price per kg is very high. The actual cost per tracer test is not very high since the injected volume is very small. The analysis is moderately priced since the price is per sample and does not regard the number of metal-complexes in the sample. Toxicity is very dependent on the concentration. Metal-complexes in general are in stock solutions of 1 g/l or more to be treated carefully i.e. plastic gloves should be used and spillage should be avoided. Concentrations of metal-complexes in the range of $\mu g\ L^{-1}$ imply no health hazard (Byegård and Skålberg, 1992).

The final choice of metal-complexes to be used in the pilot study fell on four EDTA-complexes (In, Yb, Lu, Ni), two DTPA-complexes (Gd and Ho) and perrhenat (ReO_4^-).

2.1.6 Halogenated hydrocarbons

Halogenated hydrocarbons are well known ground water pollutants and a big environmental problem. Some halogenated hydrocarbons have proved to be useful as non-reactive ground water tracers. One advantage that the halogenated hydrocarbons have is very low background or no background at all under natural circumstances. Halogenated hydrocarbons in general have shown problems with sorption, breakdown, volatility and toxicity (McCarville, Bergin and Hampton, 1995). They are generally hydrophobic and are sorbed by the solid phase of aquifer materials (Ptacek and Gillham, 1992). This behaviour leads to retarded transport rates relative to the average ground water velocity and makes compound unsuitable as a non-reactive ground water tracer. Halogenated hydrocarbons have also shown problems with solubility.

Halogenated hydrocarbons were rejected as tracers in this pilot study due to problems with sorption and solubility.

2.1.7 Benzoates

Numerous fluorinated benzoic acids have been used successfully as non-reactive ground water tracers in various hydrologic environments (Bowman and Gibbens, 1992; Jones et al., 1992; Benson and Bowman, 1994; Wilson and Linderfelt, 1994). Fluorinated benzoic acids have pK_a values of 4.5 or less, which makes them anionic and soluble in ground waters. They are easy to handle and have been analysed down to 300-600 $\mu g\ L^{-1}$ levels using HPLC with UV detection (e.g., Bowman and Gibbens, 1992). Attempts

have also been made to use a column pre-concentration of the fluorinated benzoic acids (Stetzenbach et al. 1982) which has shown that the detection limit can be significantly improved. A number of fluorinated benzoic acids can be used simultaneously if chosen so that the different species does not interfere analytically with each other. Benzoic acids are readily available from any of the large suppliers of chemical compounds. The price of benzoic acids varies a lot between the different species. They are however in general more expensive than fluorescent dyes. The analysis is made with the HPLC method and the prize is somewhat higher than the analysis price of the dyes.

Very little information on the toxicity of fluorinated benzoic acids is to be found in the literature. However, references exist to the parent compound benzoic acid. Benzoic acid is used extensively in food and pharmaceutical products (Stetzenbach and Farnham, 1994). The American Food and Drug Administration have classified benzoic acid as GRAS (Generally Recognised as Safe) as an antimicrobial and as a food additive.

The benzoic acids chosen for the pilot study were selected with respect to their transport properties and the possibility of individual detection in a tracer cocktail. The benzoic acids of choice are 2,3-difluoro benzoic acid, 2,6-difluoro benzoic acid, 3,5-difluoro benzoic acid, 2,3,4,5-tetrafluoro benzoic acid and 2,3,4,5,6-pentafluoro benzoic acid.

2.1.8 Particles and other potential tracers

Many different kinds of drifting particles have been evaluated regarding their usefulness as ground water tracers over the years. The greatest advantage of drifting particles as ground water tracers are their inactivity regarding chemical interactions with the aquifer material and their precise detectability at very high dilution. The disadvantages are unfortunately retention due to filter effects and the laborious task of detection. There are many different kinds of drifting particles; monospherical plastic particles are one group of particles that has been shown not suitable for use in crystalline rock (Björkeström, 1993).

2.1.9 Final selection of tracers for the pilot tests

The tracer tests were performed in two separate test runs. The first test run was prior to the literature study and therefore only included readily available tracers that had been used in other tests in granitic bedrock (Table 2-3). The dye tracer Uranine (Sodium Fluorescein) was used as reference tracer in all tests. In the first test a total of eight tracers (Table 2-3) were used of which six were rare earth metal-complexes.

Table 2-3: Tracers used in the first pilot tracer tests.

Tracer	Type
Phloxine B	Fluorescent dye
In-EDTA	Metal-complex
Yb-EDTA	Metal-complex
Lu-EDTA	Metal-complex
Ni-EDTA	Metal-complex
Gd-DTPA	Metal-complex
Ho-DTPA	Metal-complex
ReO_4^-	Ion

The non-reactive tracers that were used in the second test run were decided upon after the literature study was completed. This run included three separate pilot tracer tests with somewhat different equipment set-ups.

The first two pilot tracer tests of the second test run included equipment and tracers supplied by SOLEXPERTS and HYDROISOTOP GmbH, Switzerland. The main focus on these tests was the use of Helium (^{3}He) and a mixture of dyes. The final tracer test was focused on a selection of fluorinated benzoic acids. The tracers of choice for the second step are presented in Table 2-4.

Table 2-4: Tracers used in the second pilot tracer test.

Run #	Tracer	Type
1	Helium-3	Environmental isotope
2	Helium-3	Environmental isotope
	Deuterium	Environmental isotope
	Eosin	Fluorescent dye
	Sulforhodamine G	Fluorescent dye
	Pyranine	Fluorescent dye
	Dimethylfluorescein	Fluorescent dye
	Naphtionate	Fluorescent dye
	UV-1	Fluorescent dye
3	Rose Bengal	Fluorescent dye
	2,3-difluoro benzoic acid	Fluorinated benzoic acid
	2,6-difluoro benzoic acid	Fluorinated benzoic acid
	3,5-difluoro benzoic acid	Fluorinated benzoic acid
	2,3,4,5-tetrafluoro benzoic acid	Fluorinated benzoic acid
	2,3,4,5,6-pentafluoro benzoic acid	Fluorinated benzoic acid

3 Experimental set-up

3.1 Site description

The TRUE-1 site is located at 2950 m tunnel length at a depth of about 400 m below sea level in the Äspö HRL. The site includes five boreholes, KXTT1 – T4 and KA3005A, cf. Figure 3-1. The characterisation work at the site identified two potential candidate features for tracer tests, Features A and B, cf. Winberg (*ed*), (1996). Feature A was selected for the TRUE-1 tracer tests and about 20 different tracer test configurations have been used in this feature. In Feature B only one preliminary tracer test (PTT) was performed as a part of the characterisation programme, cf. Winberg (*ed*), (1996). This test identified a fast flow path between the two 2.5-m packer isolated sections KXTT3:R3 → KXTT4:R4.

The PTT test showed a high mass recovery (92%) of the injected tracer and a short mean travel time (37 minutes) over the 3.2-m distance between injection and sampling points. A summary of measured and evaluated data from the flow path is given in Table 3-1. It should also be noted that the packer positions and length of the packed-off intervals have been changed since the PTT-tests. The volume data given in Table 3-1 represents the current values. These data together with the fact that the site was still instrumented after the recently concluded TRUE-1 tracer tests made it ideal for performing some pilot tracer tests with new tracers.

Table 3-1: Measured and evaluated data from PTT for the flow path KXTT3:R3 → KXTT4:R4 in Feature B at the TRUE-1 site.

Parameter	Value	Comments
Volume of injection system KXTT3:R3	5252 ml	For section 8.92-11.42 m
Volume of withdrawal system KXTT4 R4	5252 ml	For section 8.42-10.92 m
Travel distance	3.19 m	Geometric
Longitudinal dispersivity	0.35 m	From model fitting
Equivalent fracture aperture	$1.6 \cdot 10^{-4}$ m	Calculated
Flow porosity	$2.3 \cdot 10^{-5}$	Calculated
Tracer mass recovery	92%	Calculated

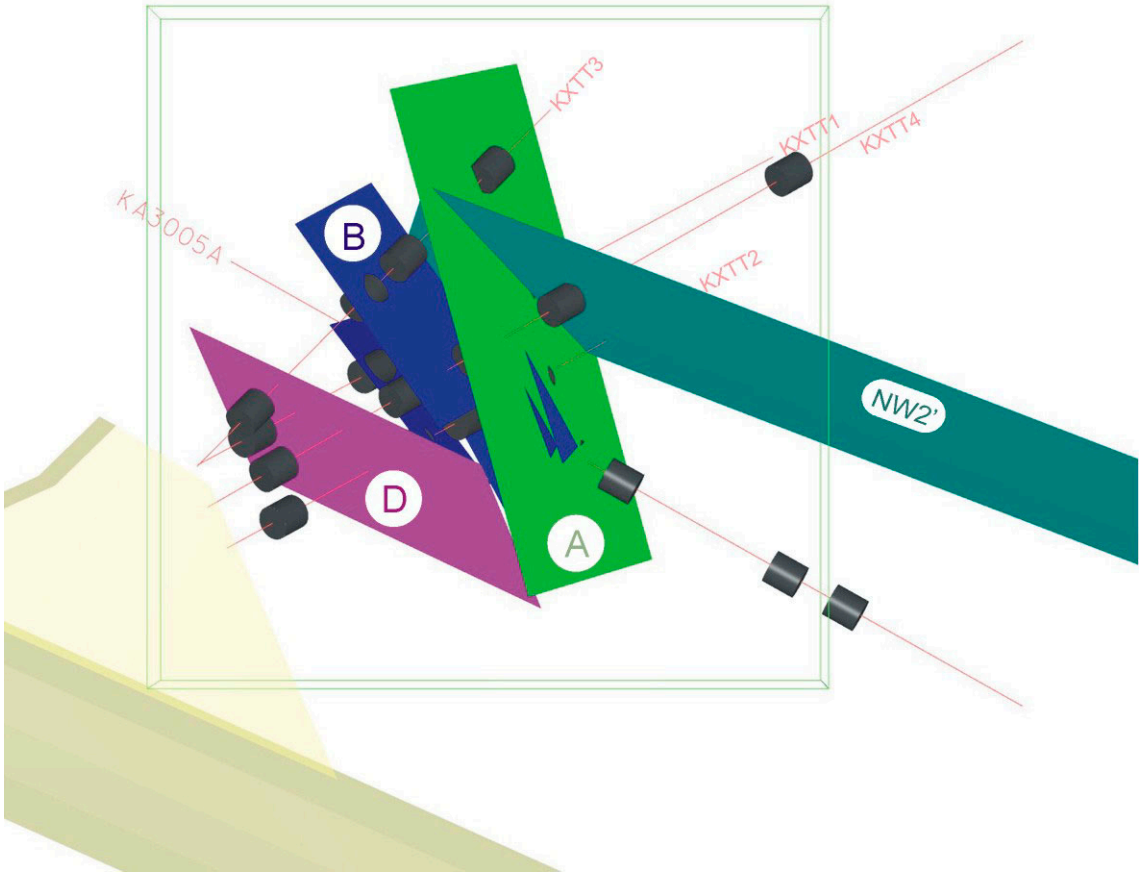


Figure 3-1: *Overview of the TRUE-1 site including boreholes, packers and interpreted structures.*

3.2 Equipment and tracers used

3.2.1 Borehole equipment

Each borehole in the TRUE-1 array is instrumented with 4-5 inflatable packers such that 4-5 borehole sections are isolated. All isolated borehole sections are connected to the Hydro Monitoring System (HMS) through data loggers. Each of the sections used as injection or sampling sections are equipped with three nylon hoses, two with an inner diameter of 4 mm and one with an inner diameter of 2 mm. The two 4-mm hoses are used for injection, sampling and circulation in the borehole section whereas the 2-mm hose is used for pressure monitoring.

The borehole sections in Feature B that were used for the tracer tests are not equipped with any volume reducing dummies.

3.2.2 Injection equipment

The pilot tracer tests were performed using the equipment set-ups for tracer tests previously used in the TRUE-1 tests. A schematic drawing of the tracer injection equipment is shown in Figure 3-2. The basic idea is to create an internal circulation of the borehole fluid in the injection borehole. The circulation makes it possible to obtain homogeneous tracer concentration inside the borehole section and to sample the tracer concentration outside the borehole in order to monitor the dilution of the tracer with time.

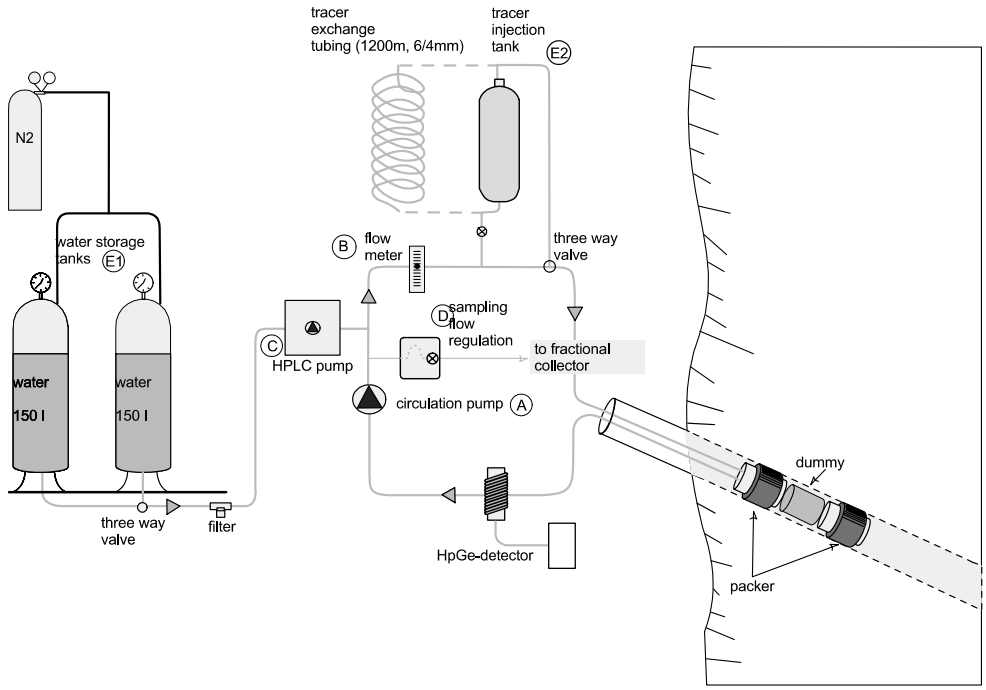


Figure 3-2: *Schematic drawing of the injection system at the TRUE-1 site.*

The circulation is controlled by a pump with variable speed (A) and measured by a flow meter (B). Tracer injections are made directly into the circulating loop with a HPLC plunger pump (C). The tracer solution in the circulation loop can be replaced with unlabelled water by switching the three-way valve such that the circulating water passes through a long (1200 m) tube filled with unlabelled water. The tracer solution then enters from one side of the tube and unlabelled water enters the circulation loop from the other side of the tube.

The tracer concentration in the injection loop is measured by sampling and subsequent laboratory analysis. The sampling is made by continuously extracting a small volume of water from the system through a flow controller (constant leak) to a fractional sampler (D). During the two tests including Helium on-line detection equipment for Uranine was used replacing the HpGe detector in Figure 3-2, cf. Chapter 3.2.3.

Water from Feature B used for the tracer exchange was collected prior to the tracer injections and stored in a separate pressurised vessel (E1) under nitrogen atmosphere. Further details about the equipment are given in Andersson, (1996).

3.2.3 Sampling and detection equipment

The sampling system is based on the same principle as the injection system, namely a circulating system with a circulation pump and a flow meter, cf. Figure 3-3. In this case however, water is withdrawn from the borehole with a constant flow rate by means of a flow regulation unit. This unit consists of a mass flow meter coupled to a motorised valve enabling a fast and accurate flow regulation.

The sampling is made with two independent systems, a ”constant leak” system collecting samples (same as in the injection loop) integrated over some time (5-100 minutes) and a 24-valve sampling unit collecting samples at discrete points in time.

After sampling, the pumped water is led through a nylon vessel where the water is degassed. The reason for this is that measurements of dye tracer content is made by an in line field fluorometer. As fluorometry is an optical method, gas bubbles need to be removed in advance or else they will create a fictive background content of the dye tracer. Hence, the degassed water is pumped from the degassing vessel through the field fluorometer and further to waste drain.

The existing fluorometer was also complemented with a fibre optic fluorometer during the Helium tests performed by SOLEXPERTS. One flow through cell was installed into the injection interval circuit. The second cell was implemented into the extraction flow line. As light source, an Argon laser (blue light 488 nm) was utilised. A beam splitter divides the laser beam; hence two optical quartz fibres can be connected to the light source. The emitted light of the fluorescence tracer is transferred by a second optical quartz fibre to the analysis device, which is equipped with a high voltage power supply, an amplifier and two photomultipliers. The signal of the emitted light is proportional to the tracer concentration. The device was developed and manufactured by SOLEXPERTS and routinely used for several years at the GTS Migration experiment (Frick et al., 1992).

The tracer technique utilising dissolved He as tracer and a commercial He leak tester (Balzers HLT 150) for on-line He detection is described in Chapter 4. In order to avoid high and possibly unstable tracer background of the pumped ground water, the isotope ^{3}He was used as tracer. The ^{3}He concentration of the ground water at the test-site was below the detection limit of the leak detector.

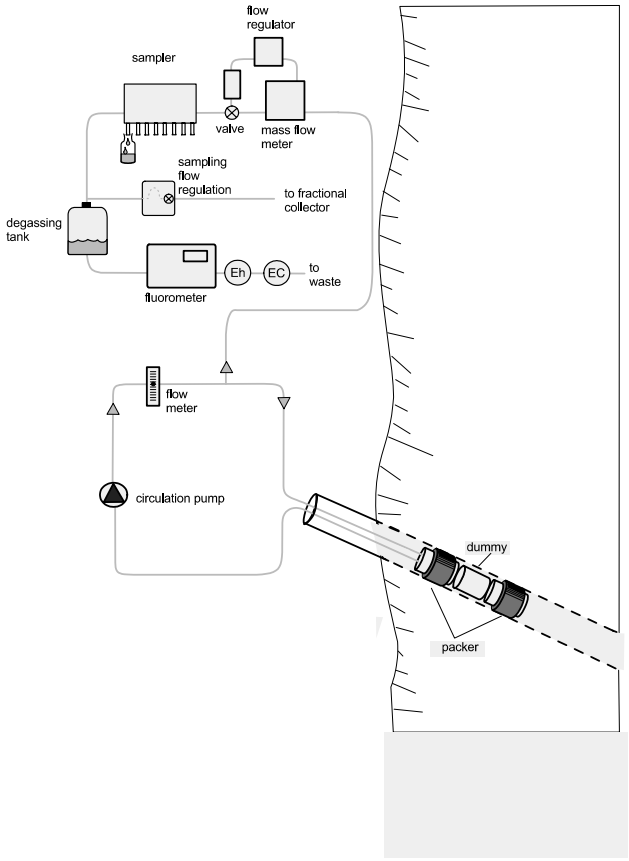


Figure 3-3: *Schematic drawing of the sampling system at the TRUE-1 site.*

3.3 Injection procedure

The tracer stock solution (100 ml) for the test without Helium was prepared at the GEOSIGMA AB Laboratory in Uppsala. The new tracers that were to be studied were mixed with Uranine which was used as a reference. The tracer solution bottle was placed on a scale so that the actual injected volume could be calculated at the end of the injection. The injection was made directly into the circulating loop as the HPLC plunger pump was started, see Figure 3-2.

The injection of the tracer solution was performed as a finite pulse injection with a length of two and a half hours in the first pilot tracer test and a length of two hours in the second. After the pulse injection the tracer solution was exchanged with unlabelled water as described in Section 3.1.2. The exchange procedure lasted for 51 minutes in both tracer tests. Before the exchange the unlabelled water in the long tube had been pressurised by adding water with the HPLC plunger pump until the pressure in the section was reached.

The injection procedure during the tests including Helium are described in Chapter 5.2

3.4 Sampling and detection procedures

The injection concentrations and the concentrations in the pumped water were monitored using the equipment described in Chapters 3.2.2 and 3.2.3. The decrease in injection concentration was measured by sampling for Uranine with samples taken every second minute during the initial 22 minutes of injection, and then every 15 minutes until the start of the exchange. The sampling frequency was then increased again in steps up to 60 minutes.

The sampling in the pumping borehole was performed using the two independent sampling systems described in Chapter 3.1.3. The ”constant leak” system was set to sample the pumped water every five minutes until the start of the exchange. The sampling frequency was then gradually increased to 60 minutes. The 24-valve sampling unit was set to sample every ten minutes for the first four hours. The sampling frequency was then gradually increased to 60 minutes. The sampling was finished after about 40 hours of elapsed time.

The analysis of the water samples was made using several different techniques besides the earlier mentioned in-line measurements of Helium and Uranine. The dye tracers Uranine, Phloxine B and Rose Bengal in the tests without Helium were analysed by spectrofluorometry using a Jasco FP-777 at GEOSIGMA Laboratory in Uppsala. All water samples were buffered to a pH of 8 to 9 before the analysis was made. A calibration curve for the dye tracer in question was loaded into the spectrofluorometer. The excitation wavelength used for Uranine was 493,0 nm and the emission wavelength was 515,0 nm. The excitation and emission wavelengths for Phloxine B were 542,5 nm and 558,0 nm respectively and for Rose Bengal 552,5 nm and 568,0 nm respectively.

The analysis of a complex mixture of fluorescent tracers as applied is only possible with advanced techniques like a HPLC procedure, which was developed at HYDROISOTOP GmbH for this purpose. The HPLC analysis was made with a HP-1090 system with automated sample supply. The column used was a Kromasil C18, 5µ, 125×4,6 mm and the eluent was an alkaline buffer/acetonitril-mix in gradient mode. The detector was a Shimadzu RF 551 S fluorometer, which could be switched automatically to the desired wavelengths. However, not all of the applied tracers can be determined with the used HPLC procedure. UV1 and Pyranine can at the present used technique not be determined by HPLC because they are not retarded on the chromatographic column. As a support for validation of the results and for analysis of UV1 and Pyranine, advanced spectrofluorometric measurements were performed. The used detection device was a spectrofluorometer, PERKIN-ELMER 203. The measuring method required pH-adjustment of the samples. The pH-adjustments were made to eliminate the disturbing effects that Uranine have on Pyranine.

- HPLC procedure: Naphthionate, Uranine, Dimethylfluorescein, Eosin and Sulforhodamine G.

- Spectrofluorometry: Naphthionate, UV1 and Pyranine.

Deuterium was measured as hydrogen by an isotope ratio mass spectrometer, type Delta, MAT Finnigan. The hydrogen was produced after reduction of water by manganese in a closed system.

High resolution ICP-MS at the SGAB Laboratory in Luleå was used in the analysis of the metal-complexes.

None of the methods proposed in the literature was possible to apply for the low concentrations of fluorinated benzoic acids obtained in the present experiment. As a sub-project and in cooperation with Analycen AB, Lidköping, Sweden, development of a new improved detection method was performed. The method consisted of a solid phase extraction (SPE) column pre-concentration in combination with a HPLC separation of the different tracer and a MS/MS detection. Details of the method are given in Appendix 4.

4 Results and interpretation of the pilot tracer tests without Helium (GEOSIGMA)

4.1 Log of events

The tracer test period on site at Äspö HRL described in this report started on January 27th, 1999 with the preparations for the pre-test and ended on March 17th, 1999 when the second radially converging tracer test was aborted. The tracer injections and the pumping were performed without major disturbances. The log of events is presented in Table 4-1.

Table 4-1: Log of events during the tracer test period.

Day	Time	Event
990126	10.40	Start pumping KXTT4 R4, Q=0.075 l/min
990127	9.30	Start tracer injection KXTT3 R3, pre test
990201	16.28	Stop tracer test, water sampling aborted
990202	11.15	Start tracer injection KXTT3 R3, first pilot tracer test
990204	12.45	Stop tracer test, water sampling aborted
990303	15.00	Start tracer injection KXTT3 R3, second pilot tracer test, run #1, SOLEXPERTS
990304	9.23	Stop tracer test, water sampling aborted, SOLEXPERTS
990304	15.02	Start tracer injection KXTT3 R3, second pilot tracer test, run #2, SOLEXPERTS
990305	9.30	Stop tracer test, water sampling aborted, SOLEXPERTS
990315	16.20	Start tracer injection KXTT3 R3, second pilot tracer test, run #3
990317	7.00	Stop tracer test, water sampling aborted
990317	7.46	Close pressure valve KXTT3 R3
990317	11.22	Close pressure valve KXTT4 R3

4.2 Tracer injections

The fifteen tracers used are listed in Table 4-2. The decrease in tracer concentration versus time was used to calculate the flow rates through the borehole by plotting the natural logarithm of concentration versus time. Theoretically, a straight-line relationship exists between the natural logarithm of the relative tracer concentration (C/C_o) and time (t):

$$Q_{bh} = -V \cdot \Delta(\ln \cdot (C / C_0) \cdot t^{-1})$$

where Q_{bh} (m^3/s) is the groundwater flow rate through the borehole section and V is the volume of the borehole section (m^3).

Table 4-2: Mean tracer concentrations during the 2-2.5 hour injection in the injection loop for the different tracers used in the study.

Tracer #	test	Tracer	Mean concentration (mg/l)
1		Uranine	5.395
1		Phloxine B	7.078
1		In-EDTA	8.06
1		Lu-EDTA	7.43
1		Ni-EDTA	16.6
1		Yb-EDTA	7.82
1		Gd-DTPA	7.13
1		Ho-DTPA	8.47
1		ReO_4	5.44
2		Uranine	6.316
2		Rose Bengal	7.778
2		2,3-DFBA	11.2
2		2,6-DFBA	12.85
2		3,5-DFBA	27.75
2		2,3,4,5-TEFBA	10.8
2		2,3,4,5,6-PFBA	11.75

The injection concentrations for the tracers used in the first test are normalised to the mean tracer concentration during the injection and plotted in the Figure 4-1. The flow rate was determined from the dilution of Uranine (Figure 4-2). This flow rate was used to calculate the mass fluxes and the recovery. The calculated injection flow rate for Uranine (compensated for sample volumes) was 68.1 ml/h in the first tracer test. The calculation of the injection flow was made using concentration values from t=5.68 hours to t=47.93 hours.

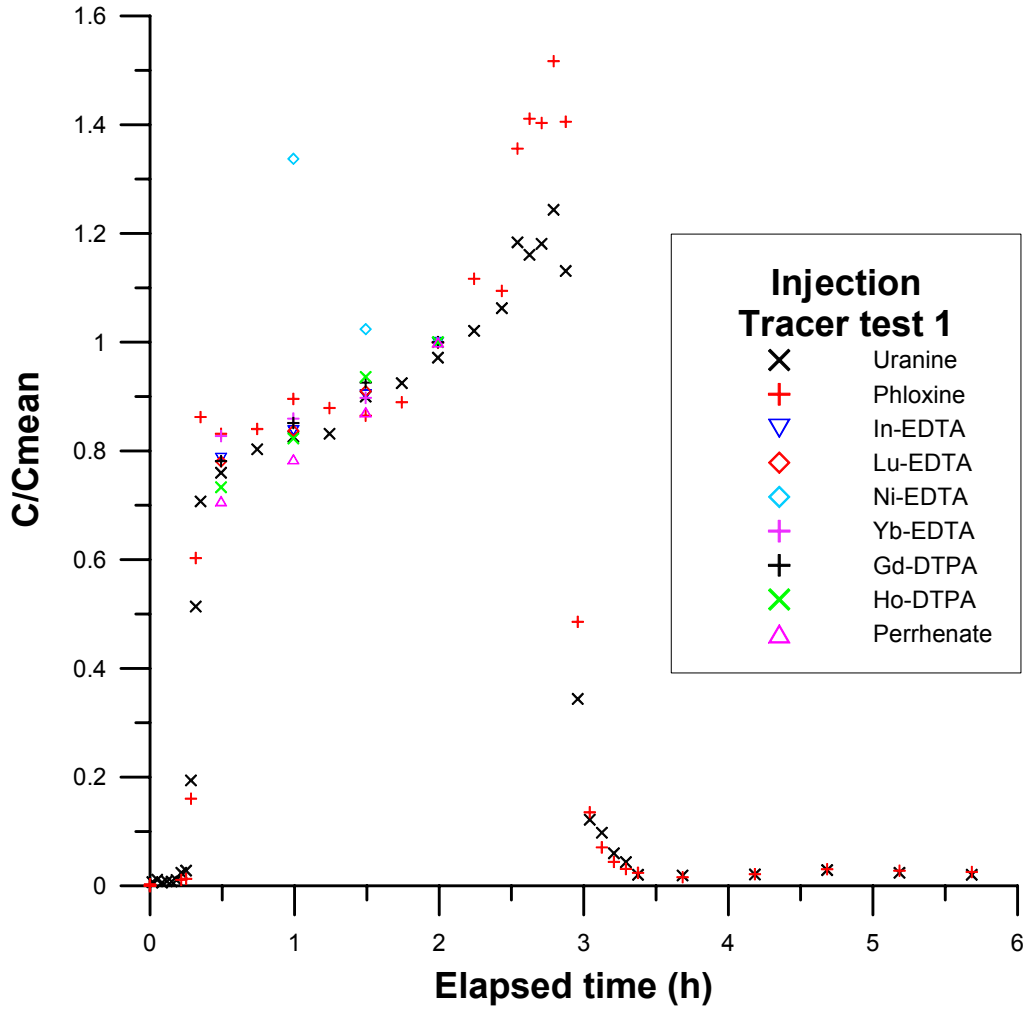


Figure 4-1: *Tracer injection concentrations normalised to the mean concentration during the injection in section KXTT3 R3 during the first 23 hours of the first tracer test.*

All tracers except Phloxine and Ni-EDTA seem to follow the reference tracer Uranine closely during the injection. The Phloxine concentrations seem to give higher values compared to Uranine and also to vary quite a lot. The normalised injection curve for Ni-EDTA has a completely different shape than any of the other injected tracers. The first measurement of Ni-EDTA has a C/Cmean value that is almost twice as large as any other C/Cmean. Therefore the first Ni-EDTA value is not plotted in Figure 4-1 but also the other values differ significantly.

The time period from the start of the injection until 3.5 hours requires some comments. The tracer concentration in the borehole section usually reaches an equilibrium concentration before the exchange is made. This is not the case in Figure 4-1 where it can be seen that the tracer concentration increases with time. The reason for this may be the fact that the borehole section volume is quite large as it is not equipped with volume reducing dummies. The lack of dummies in combination with a large borehole section decreases the rate of mixing in the section. After 2.5 hours of injection the tracer solution is exchanged with unlabelled water as described in Section 3.1.2. It is clear from Figure 4-1 that the exchange procedure was quite effective.

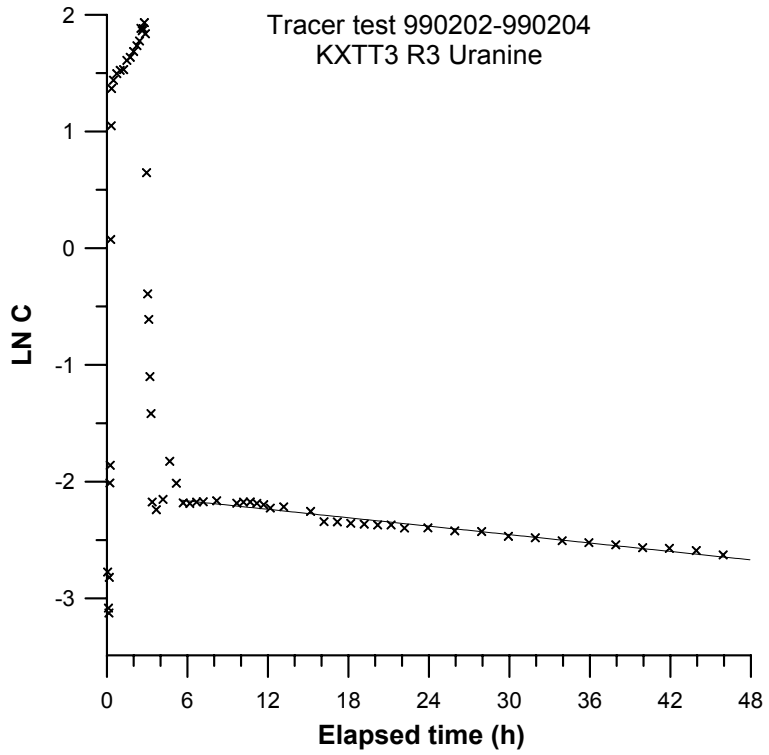


Figure 4-2: *Tracer injection concentration (lnC) versus elapsed time, t(h), for Uranine in the injection section KXTT3 R3 during the 48 hours of the first tracer test.*

The injection concentrations for the tracers used in the second test normalised to the mean tracer concentration during the injection and plotted in Figure 4-3. The flow rate was determined from the dilution of the Uranine (Figure 4-4). This flow rate was used to calculate the mass fluxes and the recovery. The calculated injection flow rate for Uranine (compensated for sample volumes) was 78.4 ml/h in the second tracer test. The calculation of the injection flow was made using concentration values from t=9.17 hours to t=38.03 hours

The normalised injection curves of Rose Bengal and the benzoic acids differ from that of Uranine (Figure 4-3). The injection concentration of Rose Bengal well exceeds that of Uranine. The time period from the start of the injection until the exchange requires some comment. It can be seen in Figure 4-3 that the tracer concentrations in the borehole section in the second test increases with time as in the first test. The reasons, as mentioned earlier, is most likely the fact that the borehole section is not equipped with volume reducing dummies and the volume of the borehole section is therefore rather large. The injection curves of the benzoic acids in Figure 4-3 are made using only five measurements. Due to the few measurements a straight line interpolation between the first and second measurements has been made to estimate the injection curves of the benzoic acids. After two hours the injection is aborted and the tracer solution is exchanged with unlabelled water as described in Section 3.1.2.

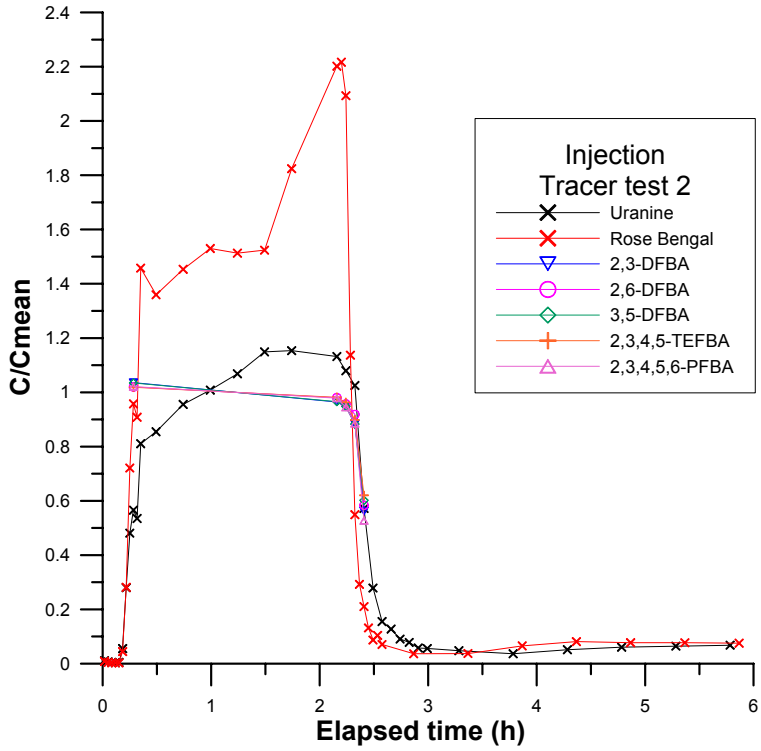


Figure 4-3: *Tracer injection concentrations normalised to the mean concentration during the injection in section KXTT3 R3 during the 38 hours of the second tracer test.*

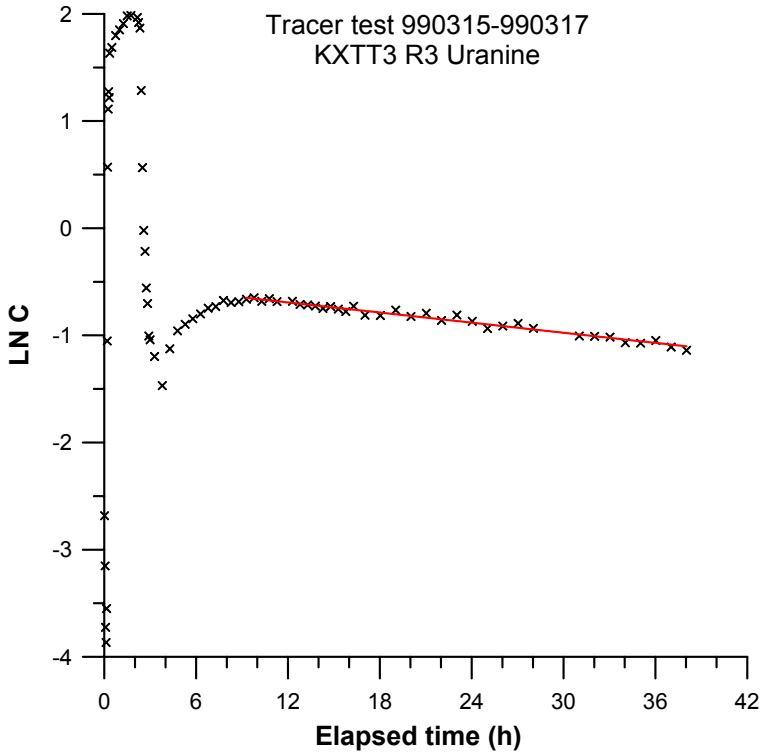


Figure 4-4*: Tracer injection concentration (lnC) versus elapsed time, t(h), for Uranine in the injection section KXTT3 R3 during the 38 hours of the tracer test.*

4.3 Tracer breakthrough

4.3.1 Tracer breakthrough data interpretation

First tracer test

The analysis of the metal-complexes and ReO_4^- with high resolution ICP-MS was repeated three times so that the instrumental spread could be calculated. The spread represents the sample standard deviation. Figure 4-5 is a representative example of the distribution and size of the sample standard deviation.

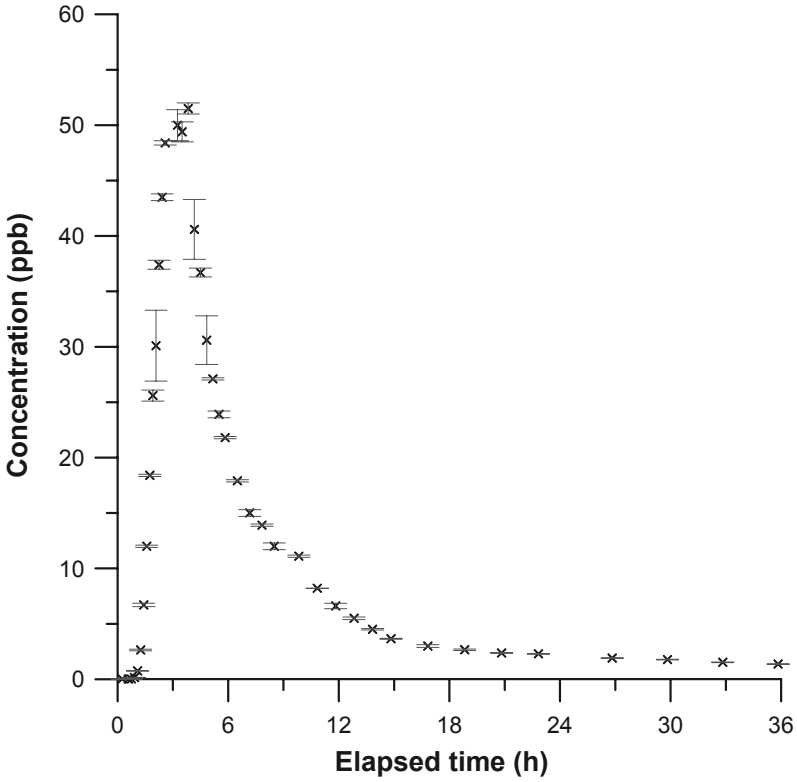


Figure 4-5: *Concentration of Gd-DTPA in the analysed water samples as a function of time. The error bars show the sample standard deviation.*

Tracer breakthrough in the pumping section was monitored for all the injected tracers. The breakthrough curves (Figure 4-6 and a close-up of the first 12 hours in Figure 4-7) show one distinct and high peak reflecting the shape of the injection function. The plots in Figure 4-6 show concentrations that are normalised to the mean concentration during the injection phase of the test. The normalisation is made in order to get a good comparison between the different species.

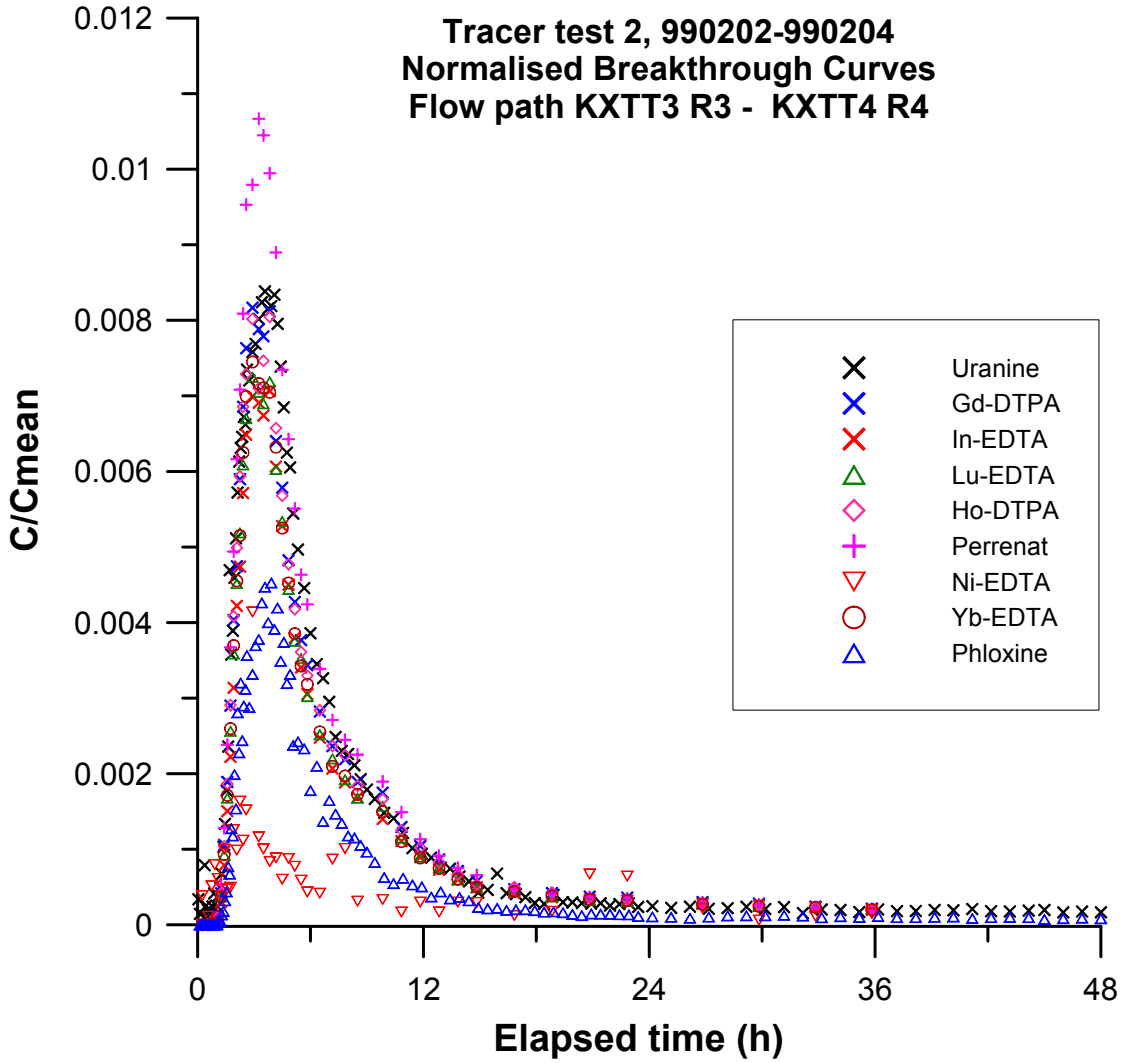


Figure 4-6: *Tracer breakthrough curves for the tracers in the first tracer test. Tracer concentrations are normalised to the mean tracer concentration during the injection phase.*

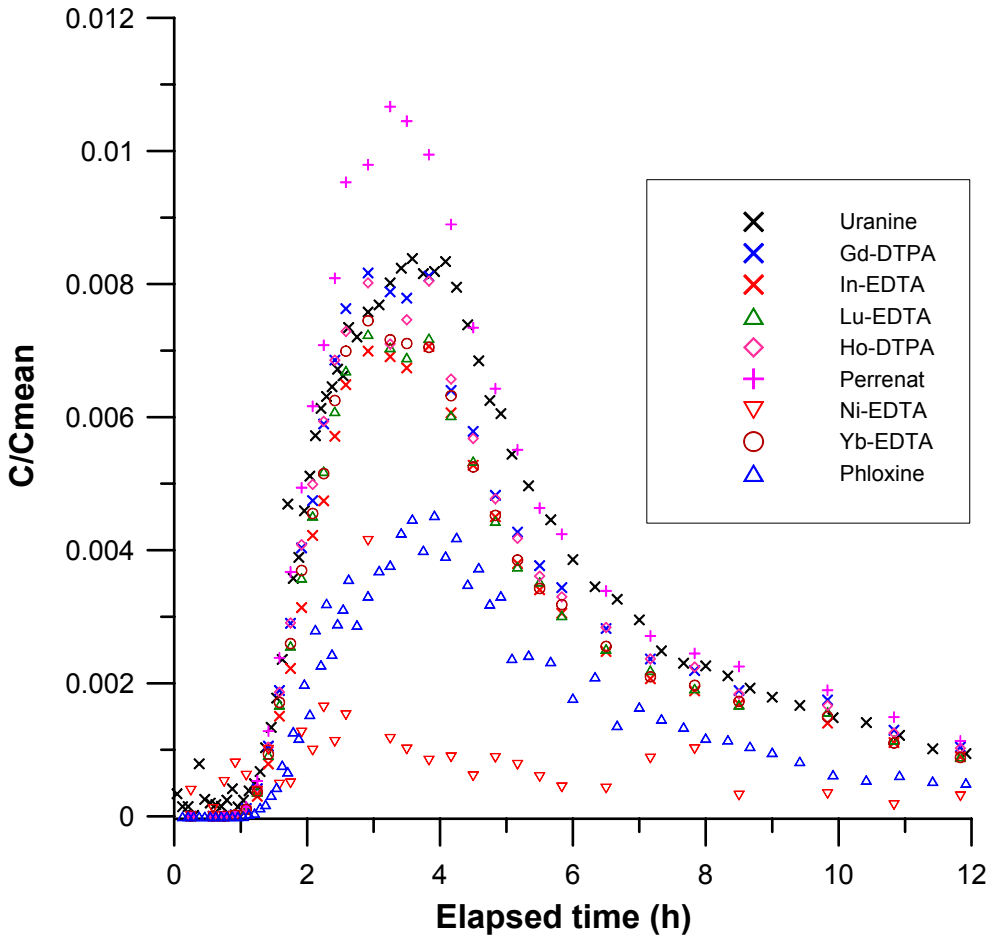


Figure 4-7: *Tracer breakthrough curves for the first 12 hours of the first tracer test. The tracer concentrations are normalised to the mean tracer concentration during the injection phase.*

Figures 4-6 and 4-7 show that the breakthrough curves of the dye tracer Phloxine and metal-complex Ni-EDTA are clearly divergent from that of Uranine. The breakthrough curve of Phloxine, the rise as well as the peak and the recession, is considerably lower than that of Uranine. This indicates that Phloxine is a sorbing tracer. Another indicator of this is the fact that Phloxine coloured the tubing in the injection system during the injection process. The breakthrough curve of Ni-EDTA has a completely different appearance than any of the other curves. This may partly be due to the fact that the background of Ni is high. The high background is mainly due to contamination by the alloy in the metal equipment in- and outside the borehole. The low peak in the breakthrough curve indicates that the metal-complex Ni-EDTA is sorbing.

The breakthrough curves the metal-complexes, except that of Ni-EDTA, has its rise and peak approximately simultaneous to that of Uranine. The breakthrough recessions of the metal-complexes are in general faster than that of Uranine during the first five hours of the recession. Thereafter the breakthrough recessions of the metal-complexes are similar to that of Uranine.

Second tracer test

Tracer breakthrough in the pumping section was monitored for all the injected tracers. The plots in Figure 4-8 show the breakthrough curves of Uranine, Rose Bengal and the benzoic acids normalised to the mean concentration during the injection phase of the tracer test. The normalisation is made in order to get a good comparison between the different species. The breakthrough curve of Uranine has one distinct and high peak reflecting the shape of the injection function. The breakthrough curve of Rose Bengal has two very small and not very distinct peaks and does not at all reflect the injection function. The breakthrough curves of the five benzoic acids all have its rise approximately simultaneous to that of Uranine. The time of peak value may coincide with that of Uranine, this is however uncertain due to the fact that no analysis of the benzoic acids has been made at the time for the peak value of Uranine. There are also differences in the breakthrough curves between the different benzoic acids. The benzoic acids 2,3-DFBA, 2,6-DFBA and 2,3,4,5-DFBA all have very similar breakthrough curves (Figure 4-8) while 3,5-DFBA has significantly lower concentration levels and 2,3,4,5,6-PFBA has higher concentration levels. There is a low background concentration of Uranine during the second tracer test. This is a result of the previous tracer tests performed at the site.

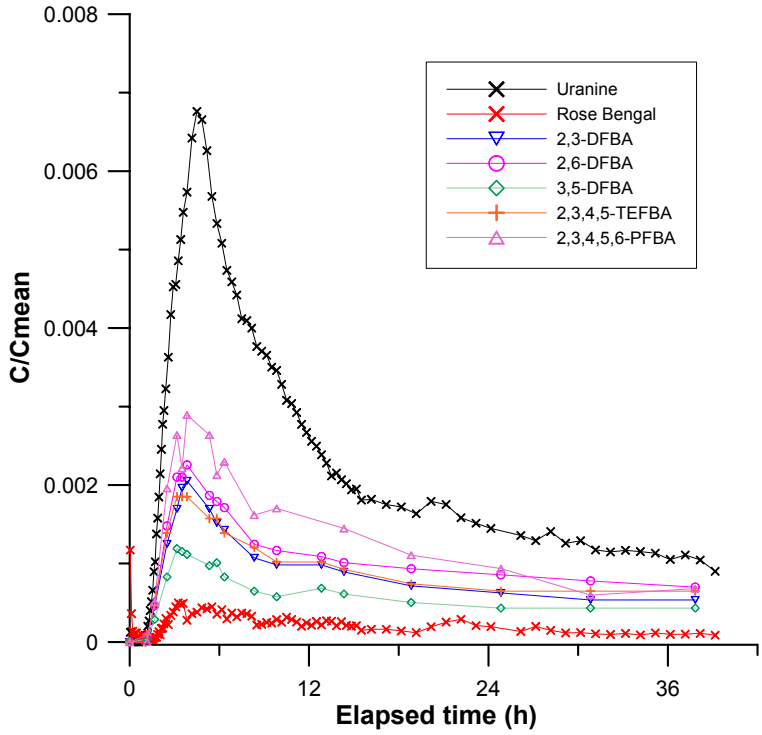


Figure 4-8: *Tracer breakthrough curves for the second pilot tracer test. The tracer concentrations are normalised to the mean tracer concentration during the injection phase.*

4.3.2 Tracer mass recovery

First pilot tracer test

In the first pilot tracer test the calculated tracer mass recovery for Uranine was 100%. The recoveries of the other tracers are somewhat more uncertain due to the very few analysis made in the injection loop (four samples). Under the assumption that the same relative mass of the metal-complexes is injected as for Uranine, the recoveries for the majority of the metal-complexes are somewhat lower than that of Uranine (Table 4-3). The high peak value of ReO_4^- is well reflected by the (too) high recovery. This high recovery is most likely a result of uncertainties in the injection function. The sample standard deviation of the concentration during the injection is higher for ReO_4^- than for any of the other metal-complexes. The mean concentration of ReO_4^- during the injection is probably overestimated.

Table 4-3: Tracer mass recoveries in the first tracer test calculated by integration under the assumption that the same relative mass of the metal-complexes is injected as for Uranine.

Tracer	Recovery (%)
Uranine	100
Phloxine	49
In-EDTA	81
Lu-EDTA	83
Ni-EDTA	29
Yb-EDTA	84
Gd-DTPA	93
Ho-DTPA	91
ReO_4^-	110

Second pilot tracer test

In the second pilot tracer test the calculated tracer mass recovery for Uranine was 100%. The recoveries of the benzoic acids are somewhat more uncertain due to the very few analysis made in the injection loop (five samples). Under the assumption that the same relative mass of the benzoic acids is injected as for Uranine, the recoveries for the benzoic acids are significantly lower than that of Uranine, 26%-56% (Table 4-4). The mass recovery of Rose Bengal is also calculated under the assumption that the same relative mass is injected as for Uranine. The more or less peak-less breakthrough curve of Rose Bengal (Figure 4-8) is well reflected by the very low recovery (10%). The low recovery is most likely due to sorbing and/or precipitation. Sorption on the walls of the tubing could also be directly observed during the field test.

Table 4-4: Tracer massrecoveries in the second tracer test calculated by integration under the assumption that the same relative mass of the benzoic acids is injected as for Uranine.

Tracer	Recovery (%)
Uranine	100
Rose Bengal	10
2,3-DFBA	38
2,6-DFBA	47
3,5-DFBA	26
2,3,4,5-TEFBA	40
2,3,4,5,6-DRBA	56

5 Performance and results of the pilot tracer tests with Helium, Deuterium and a mix of fluorescent dyes (SOLEXPERTS)

5.1 Laboratory tests on the use of Helium

A tracer test technique utilising dissolved He (^{3}He and ^{4}He) as tracer and a commercial He leak tester for on-line He concentration detection was developed in the framework of the radio-nuclide migration experiment at the Grimsel Test Site, Switzerland (Eikenberg et al., 1992, Frick et al., 1992). The concept of the on-line He detection is based on a flow-through cell with two chambers separated by a highly gas-permeable membrane. The fluid passes through one chamber. In the second chamber, the He leak tester creates a vacuum. The dissolved gases in the fluid are extracted through the gas-permeable membrane into the vacuum chamber, which is connected to the mass spectrometer of the He leak tester. The He concentration in the fluid is proportional to the leak rate through the membrane as long as fluid flow rate and pressure are constant. The transfer of the He tracer equipment to the Äspö HRL required a few equipment modifications. The two most critical items for feasibility of the planned He tracer tests at the Äspö HRL are the high static heads and the loss of He in polyamide flow lines.

5.1.1 High static heads

The existing silicon membrane in the He flow-through cell is specified for maximal 3 bar working pressure. At the True Block Scale site, pore-water pressures are measured up to 45 bars. A new membrane had to be evaluated for pressures up to 60 bars. The requirements for the membrane were as follows:

- High gas permeability (ensures maximal sensitivity and low detection limit)
- Linear relation between He concentration and He leak rate at stable flow rate and working pressure)
- Working pressures up to 60 bars

The silicon membrane between the flow and vacuum chamber of the flow- through cell was removed and replaced with 0.2-mm thick PTFE (Teflon) foil. The membrane was tested up to 70 bars working pressure. Compared to the silicon membrane, the gas permeability of the Teflon membrane was reduced approximately by a factor of 2. Calibration runs (test set-up Figure 1) using various dosage rates of He saturated water (He concentrations) showed a linear behaviour of He concentration versus He leak rate signal.

5.1.2 He loss in polyamide flow lines

At the Grimsel Test Site, stainless-steel flow lines were used for tracer injection and pumping out of the extraction interval. The packer systems at the True Block Scale Site are equipped with polyamide flow lines (od. 6mm id. 4mm). Therefore, possible He loss through polyamide flow lines had to be investigated (He diffusion through lines). Eight laboratory tests were performed. The test set-up is represented in Appendix 1, Figure 1. The tests are summarised in Table 5-1.

Table 5-1: Test of He diffusion through polyamide lines

	Test1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Flow rate [ml/min]	75	75	75	75	150	800	147	147
Residence time in polyamide line [min]	16.75	16.75	16.75	9.42	8.37	1.57	8.54	8.54
Dosage rate [ml/min]	2	2	2	2	5	10	5	5
Pressure [bar]	14	14	14	14	2	2	12	18
Leak rate without lines [mbarl/sec]	3.6E-8	3.6E-8	3.6E-8	3.6E-8	3.25E-8	1.30E-8	3.85E-8	3.85E-8
Leak rate with 100 m polyamide line (6/4mm) [mbarl/sec]	2.8E-8	2.8E-8	2.8E-8	3.1E-8 [3)]	3.05-8	1.30E-8	3.45-8	3.4E-8
Difference in leak rate [mbarl/sec]	0.8E-8	0.8E-8	0.8E-8	0.5E-8	0.2E-8	0.0E-8	0.4E-8	0.45E-8
Difference in %	22	22	22	14	6	0	10	11.7
Note		[1)]	[2)]	[3)]	[4)]	[5)]	[6)]	[7)]

[1)] repetition of test 1 to check reproducibility

[2)] polyamide line in water filled vessel

[3)] 3mm inner diameter of polyamide line (reduced residence time in polyamide line, less He loss)

[4)] higher flow rate, low pressure (reduced residence time in polyamide line, less He loss)

[5)] higher flow rate, low pressure (reduced residence time in polyamide, no detectable He loss)

[6)] higher pressure (increased He loss)

[7)] higher pressure (increased He loss)

The laboratory tests showed the following results:

- Polyamide lines are not He tight
- He loss does not change when polyamide lines are submerged in water (instead of air) (Test 3)
- He-loss is strongly dependent on residence time of He-traced water in a polyamide line. At low pressure, if the residence time is less than 1.5 min, no He loss was detectable (Test 6); if the residence time is 8 min, about 6 % of He diffuse through the polyamide line (Test 5).
- He-loss depends on pressure within polyamide line. (Tests 5, 7 and 8; the higher the pressure the larger the He-loss)
- Test 2 confirmed the reproducibility of the test procedure

5.1.3 Conclusions of laboratory tests

He tracer tests are feasible at the True Block Site using the same technique as at the Grimsel Test Site taken into account:

- High pressures: A Teflon membrane in the flow-through cell (instead of a more permeable silicon membrane) enables the use of the He tracer technique up to 70 bar working pressures.
- He diffusion through polyamide flow lines: The laboratory tests showed that polyamide lines are not He tight. Possibilities to remedy this problem are:

  i) The best solution would be to replace the polyamide flow lines with stainless steel lines. When packer systems are removed and packer seats are modified, there is a good opportunity to equip tracer injection or extraction borehole sections with stainless steel lines

  ii) Minimise the residence time within the polyamide lines; short residence times can be achieved by high flow rates at the pumping site and at the tracer injection site. If the residence time within the polyamide flow line is less than 2 min, the He loss within the line is negligible. Assuming a typical pumping rate for a tracer experiment at the True Block Scale test site of 1.5 l/min and 200 m flow line (id: 4 mm), the residence time would be less than 2 min. At the pumping site, the He loss within the polyamide flow line is most likely no problem. At the injection side, a tracer dosage procedure has to be applied that is aimed at minimising residence time within the flow line to the injection interval. The tracer injection procedure applied in the pilot He tracer tests (Appendix1 Figure 2) was successful.

  iii) Quantify He loss with laboratory experiments using similar length of polyamide lines, similar pressures, flow rates and He concentrations.

  iv) A combination of i) and ii) would be the best to obtain reliable, high quality tracer test data.

5.2 Field tests

5.2.1 Objectives

- Feasibility check of He tracer technique at Äspö HRL for the True Block Scale experiments
- Evaluation of He as a conservative (non-reactive) and highly diffusive tracer
- Compatibility check of existing surface and down-hole equipment with He tracer test equipment developed at the Grimsel Test Site Migration experiment
- Feasibility check of He and Uranine on-line detection technique at Äspö HRL for the True Block Scale experiment
- Check of the conservative (non sorbing behaviour) of several dyes

5.2.2 Dipole flow field

Tracer test 1 was performed in a 4-m long flow field established between borehole KXTT3, interval R3 and borehole KXTT4, interval R4. Injection flow rate was 10 ml / min for field test 1 and 6 ml/min for field test 2 respectively. The extraction flow rate was in both tests 75 ml/min. To maximise tracer recovery the dipole flow field was kept narrow (especially at test 2) by a high ratio of extraction to injection flow rate. Pressures and flow rates were monitored using the existing data acquisition system at the test site. GEOSIGMA was in charge for the maintenance of the flow field during the tracer test.

5.2.3 Tracer dosage

Using dissolved He as tracer requires a closed tracer tank (He escapes if the labelled water comes in contact with a gas atmosphere). In order to extract labelled water, the tank is equipped with an O-ring sealed plunger, which divides the tank into two chambers (Appendix 1, Figure 2); chamber one is filled with unlabeled water and chamber two with traced water. Tracer dosage is performed by water injection into chamber 1.

Due to the polyamide flow lines, which are not perfectly He tight, of the installed packer systems, the residence time of He within the polyamide flow lines had to be minimised. Therefore, the following tracer dosage procedure was applied:

1. Dipole injection with 10 ml/min (Test 1) or 6 ml/min (Test 2) respectively; Dipole extraction with 75 ml/min (both tests).
2. Injection interval circulation with high flow rate (250 ml/min).
3. Open tracer tank bypass, tracer injection.
4. Continue circulation until first arrival of Uranine in fluorescence flow-through cell, then open fluid exchange bypass and close tracer tank bypass.

5. Monitor Uranine tracer concentration to obtain a (time shifted) tracer input function.

6. Stop fluid exchange after injection reaches Uranine background. with the following advantages:

- Minimal He loss due to minimal residence time of Helium in the lines

- Well-defined tracer input function, (concentration versus time measured, known flow rate into formation)

The injected tracer mass M(0) was calculated making the following assumptions:

- The concentration versus time distribution within the injection interval corresponds exactly to the breakthrough curve measured in the circulation line (see Appendix 1, Figure 2). The long injection interval (2.5 m) and its large volume (5.2 litres) are a disadvantage for this assumption.

- The Uranine injection function corresponds exactly to the injection function of the other tracers. This assumption is based on equal mixing and dilution of all tracers within the injection interval. The long injection interval (2.5 m) and its large volume (5.2 litres) are a disadvantage for this assumption.

- No He loss through polyamide line during tracer injection (30 m, 6/4 mm polyamide line, flow rate 250 ml/min, residence time about 1.5 min). The laboratory tests showed that residence time shorter than 2 min within polyamide lines result in negligible He loss. The test (test 6) was performed with a low pressure of two bars in the line. During the field test, the pressure was about 30 bars. It is most likely that 30 bar pressure causes some He loss.

- The dipole injection rate was exactly 10 ml/min or 6 ml/min respectively. The injection flow was monitored by a GEOSIGMA flow meter.

Taking into account all the uncertainties mentioned above, the accuracy of M(0) for all tracers and especially more accentuated for He is most likely not very high. It is not possible to make an estimation of the accuracy without investigation of all the mentioned uncertainties in detail. However, the tracer recovery of Uranine (92 % test 2) is in very good agreement with prior tracer tests using similar flow rates and the same borehole configuration (Andersson, personal communication).

5.2.4 Results

General:

The breakthrough curves of all tracers are similar except Sulforhodamine G.

Equipment:

- The on-line detection of Uranine and He is in good agreement with the measured samples.

- It was possible to distinguish and measure accurately seven dyes (Uranine, UV1, Eosin, Naphthionate, Sulforhodamine G, and dimethylfluorescein, Pyranine) within one sample using HPLC technique and spectral fluorometry.

Comparison test 1 and test 2:

- Tracer breakthrough of test 1 shows for all tracers two peaks. Two preferential pathways within the flow field are most likely an explanation. The first peak (main peak) shows its maximum in sample T4:10 (50 min after start of tracer injection), the second peak in sample T4:34 after 260 min.

- Tracer breakthrough curves of test 2 are monomodal. Test 2 dipole flow field was narrower compared to the flow field of test 1, due to the decreased injection flow rate. It is likely, that the second preferential flow path, which probably was responsible for the second test 2 peak, was not covered by the narrower test 2 dipole.

Dyes:

- Comparing the two peaks allows for describing the characteristics of the used tracers under the local conditions. All tracers with exception of Sulforhodamine G show very small differences regarding their breakthrough curve. This points out the fact that the tracers behave conservative (no or very small sorption). The dyes show differences in peak concentration ratio of peak 1 and peak 2, which can be related to well known characteristics of the different tracers. The average in the ratio of the peaks between peak 1 and peak 2 is 12.6. For the individual tracers are the following values obtained:

Naphthionate:	12.5
UV1:	14.1
Uranine:	11.9
Dimethylfl.:	11.8
Eosin:	10.5
Pyranine:	16.3
Deuterium:	11.3
Mean value:	12.6

The ratio between the height of the first and the second peak is with 14.1 for UV1, which is higher than the mean value (12.6). This could be caused by a very low sorption of this tracer. For Dimethylfluorescein and even more for Eosin the ratio is lower than the mean value. This corresponds (especially for Eosin) with a known slight tendency of these tracers to reversible sorption. The deviation of the ratio for Pyranine (16.3) may be caused by some difficulties of the analysis of this tracer in the complex mixture at lower concentration. However, it is known that this tracer is the least stable of all applied tracers. Some degradation due to light exposure could have been occurred.

The differences in ratio may to some extent be caused by differences in analytical accuracy at high and lower concentrations. It appears however very likely that the differences are based on well known slight differences in the tracer behaviour. The ranking of the ratio between peak 1 and 2 is in agreement with the knowledge of the sorptive properties of the tracers.

Helium:

- First arrival of Uranine and He is simultaneous. The simultaneous first arrival of the tracers is an indication that the early time data of the breakthrough curve is governed by advection in highly transmissive flow paths.

  Peak time of Helium compared to Uranine is delayed about 3 minutes in both tests. He peak concentration is in both tests about 30 % lower than the Uranine peak. The retardation is small, but is in agreement with the smaller peak concentration and the more pronounced tailing of He. Experimental artefacts or different transport behaviour of the two tracers can cause the lower He peak concentration compared to Uranine.

  Possible experimental artefacts are the following:

  - He loss in extraction flow line (chapter 2.2): The lab tests showed that the He loss in polyamide lines depends on residence time and pressure within the line. Based on the laboratory tests (test 1 to 3) the He loss within the extraction line during the field experiment can be extrapolated to about 8 – 12 %.

  - Uncertainty of M(0): Due to not taking into account He loss within the injection flow line during tracer injection, it is most likely that M(0) of He was overestimated.

  - Note that both possible artefacts can not explain the long tailing of He.

  Different transport behaviour:

  - More accentuated diffusion of He may have caused the longer tailing of the He breakthrough curve, which is in agreement with a smaller peak concentration compared to Uranine.

The lower He peak concentration and the lower tracer recovery are most likely caused by a combination of different diffusion processes within the fracture and experimental artefacts. However, it cannot be excluded, that the longer tail of the He breakthrough curve is caused by different input functions for He and Uranine due to different mixing within the injection interval or uncompleted exchange of traced water within the injection interval or back diffusion from polyamide lines. However, tracer tests at the Grimsel Test Site within a highly transmissive fracture showed similar results (lower He peak, more accentuated tailing). Most of the above mentioned possible artefacts can be excluded for the Grimsel experiments.

6 Laboratory study of solubility and solvent extraction

6.1 Solubility test of Fluorescein and Fluorescein derivative

6.1.1 Introduction

Sorption and/or precipitation behaviour was observed at the injection in the *in situ* experiment for the Fluorescein derivative Phloxine B and Rose Bengal. It was suspected that solubility problem may have arisen when mixing high concentrations of tracer with the highly saline Äspö groundwater. A solubility test was thus initiated in order to obtain general information about the solubility of Fluorescein and Fluorescein derivative; a group of potential groundwater tracers.

6.1.2 Experimental

Solutions were mixed with 5mM of each tracer mixed with different species according to the descriptions in Table 6-1, i.e.;

A. 50mM NaCl and 25mM $CaCl_2$, simulating the mixing of 10000 ppm tracer solution with high saline Äspö groundwater in equal proportions, i.e., the injection situation.

B. 50mM NaCl, 25mM $CaCl_2$ and 5mM acetate-buffer, giving pH=4. Chemical conditions as in A with lower pH to see if that would make it possible to inject tracer in higher concentrations without precipitations

C. 10mM acetate-buffer, giving pH=4. As in B, investigating if the precipitations formed in B could be formed only by lowering the pH, i.e., no high salinity present

D. 50mM NaCl, 25mM $CaCl_2$ and 5mM NaOH, giving pH=11.7. Chemical conditions as in A with higher pH to see if that would make it possible to inject tracer in higher concentrations without precipitations

E. 10mM NaOH, giving pH=12. As in D, investigating if the precipitations formed in B could be formed only by higher pH, i.e., no high salinity present

F. 0.5M NaCl, no $CaCl_2$ present. Only tested for the tracers that precipitated in A, to obtain an indication if the presence of Ca^{2+} is the key parameter for the solubility

G. 1M NaCl, 50mM borate buffer giving pH=9. The buffer concentration was higher than the tracer concentration. A pH close to the natural pH was obtained, i.e., only very small pH variations should thus be obtained in the injection situation with borate buffer present. It could thus be a way to avoid precipitations.

H. 1M NaCl+ 0.05M $CaCl_2$, 50mM borate buffer giving pH=9. As in G but with Ca^{2+} present.

I. 1M NaCl+ 0.05M $MgCl_2$, 50mM borate buffer giving pH=9. As in H but with Mg2+ present instead of Ca^{2+} (another divalent cation).

6.1.3 Result of the solubility tests

Table 6-1: Results of the solubility test of some fluorescent tracers.

	A 50mM NaCl 25mM $CaCl_2$	B 50mM NaCl 25mM $CaCl_2$ 5mM acetate-buffer, pH 4	C 10mM acetate-buffer, pH 4
Fluorescein (Uranine)	No precipitation	No precipitation	No precipitation
Eosin B	Precipitation	Precipitation	Precipitation
Eosin Y	Precipitation	Precipitation	Precipitation
Phloxine B	No precipitation	Precipitation	Precipitation
Rose Bengal	Precipitation	Precipitation	Precipitation
Dibromofluorescein	No precipitation	-	-
Diiodofluorescein	No precipitation	-	-
Tetrechlorofluorescein	No precipitation	-	-
Carboxyfluorescein	No precipitation	-	-
Dinitrofluorescein	No precipitation	-	-

	D 50mM NaCl 25mM $CaCl_2$ 5mM NaOH, pH 11.7	E 10mM NaOH, pH 12	F 0.5M NaCl
Fluorescein (Uranine)	No precipitation	No precipitation	-
Eosin B	Precipitation	Precipitation	No precipitation
Eosin Y	Precipitation	Precipitation	-
Phloxine B	Precipitation	Precipitation	No precipitation
Rose Bengal	Precipitation	Precipitation	No precipitation
Dibromofluorescein	-	-	-
Diiodofluorescein	-	-	-
Tetrechlorofluorescein	-	-	-
Carboxyfluorescein	-	-	-
Dinitrofluorescein			

	G 1M NaCl, 50mM borate buffer, pH 9	H 1M NaCl, 50mM borate buffer, pH 9 + 0.05M $CaCl_2$	I 1M NaCl, 50mM borate buffer, pH 9 + 0.05M $MgCl_2$
Fluorescein (Uranine)	No precipitation	No precipitation	No precipitation
Eosin B	No precipitation	Precipitation	Precipitation
Eosin Y	No precipitation	Precipitation	Precipitation
Phloxine B	No precipitation	No precipitation	No Precipitation
Rose Bengal	Precipitation	Precipitation	Precipitation
Dibromofluorescein	No precipitation	No precipitation	No precipitation
Diiodofluorescein	No precipitation	No precipitation	No precipitation
Tetrechlorofluorescein	No precipitation	No precipitation	No precipitation
Carboxyfluorescein	No precipitation	No precipitation	No precipitation
Dinitrofluorescein	No precipitation	No precipitation	No precipitation

6.1.4 Conclusions

It can be observed that several of the Fluourescein derivatives are precipitated when they are mixed in high concentrations with an electrolyte with a composition similar to groundwater. This effect is pronounced for the different Eosines and for Rose Bengal. From a chemical perspective, the results indicate that the presence of divalent cations (e.g., Ca^{2+} and Mg^{2+}) favor precipitation of these tracers and one can speculate that these cations react with different fluorescein derivative forming compounds with low solubility. However, effects are also observed that indicates that precipitation can occur due to pH variations.

When comparing the different tracers in their potential to precipitate, it is indicated that fluorescein derivative that have halogenated substitution in position 1-6 (i.e., Eosin B, Eosin Y and Rose Bengal, cf. Figure 6-1) are most suspected to precipitate. The only exception to this trend is Phloxine B, which does not seem so sensitive for precipitation in the laboratory experiment. However, in the *in situ* experiment, non-satisfying results (losses in the injection borehole) were obtained for Phloxine B.

A potential explanation for the different tracer behaviour is that substitution in position 5 makes it possible for the divalent cations to bind as a bridge between the carboxy group and the substituted halogen in position 5. Another explanation is that the many substituted halogen groups in the two aromatic side rings of Eosin B, Eosin Y, Phloxine B and Rose Bengal influences the charge distribution of the entire molecule and thereby also the pKa of the carboxyl group. Unfortunately, among the Fluorescein derivative used in the investigation, the pKa´s has only been determined for the non-substituted Fluorescein (review in Smith and Martell, 1985).

Substitution only in the single aromatic ring (position 7-10) does not seem to cause increased ability to form precipitation, as exemplified by carboxy-fluorescein and tetrachloro-fluorescein.

6.1.5 Comparing observed in situ stability with the laboratory results

Non-substituted Fluorescein (i.e., Uranine) behaves well in the laboratory solubility studies; i.e., no precipitation in any chemical environment can be observed. Solubility problems in the injection sections were not at all indicated. There is a considerable experience in injecting Uranine in high concentrations in many different type of groundwater and no reports of solubility problems have been observed.

Rose Bengal and Phloxine B were tested in the in situ experiment. After the injections, a strong red color was observed through the transparent tubing for which it took a large amount of rinsing with groundwater before the color disappeared. Concerning the Rose Bengal, the behaviour in the *in situ* experiment is consistent with the observations solubility problems in the laboratory experiment. On the other hand, the laboratory experiment mixing a concentrated solution containing Phloxine B with a synthetic groundwater gave no precipitation. In the *in situ* experiment in Stripa (e.g., Birgersson et al.1992) Phloxine B and Rose Bengal was used as tracer. Breakthrough was obtained; however with somewhat lower recovery rate compared to the tracers injected simultaneously, Dy-$DTPA^{2-}$ and ReO_4^-, respectively. A possible explanation to the more pronounced problem in the Äspö experiments is that the groundwater in Stripa had a lower concentration of Ca (18-32ppm, Albelin et al. 1987) compared to the groundwater

used in the *in situ* tracer experiment (950 ppm Ca, Säfvestad and Nilsson, 1999). This hypothesis would be consistent with the laboratory experiment observation of precipitation occurring in the laboratory experiment.

The concentrations of Rose Bengal and Phloxine B in the injection borehole was ~7mg/l for each of them; corresponding to a molar concentration of <10μM. This is considerable lower compared to the conditions applied in laboratory experiment where the tracer concentrations were a factor ~500 higher. One can therefore speculate of a formation of complex with the tracers and Ca^{2+}, as indicated by the results of the laboratory experiment. In the *in situ* situation with lower tracer concentration, this would probably give a soluble non-charged complex that could undergo adsorption, e.g., on nylon tubing as was observed in the *in situ* experiment. Accordingly, in the laboratory experiments, the concentration of the non-charged complex could be high enough to form the precipitations.

Satisfying results were found for Eosin Y in the *in situ* experiment, which is somewhat contradictory to the solubility problems observed in the laboratory experiment. Concerning the tracer Dibromofluorescein, no solubility problems could be observed in the laboratory experiment. However, Albelin et al. (1987) rejected Dibromofluorescein (Solvent Red 72) as tracer since the laboratory experiment indicated it was suspected to degrade and sorb on granite. Dimethylfluorescein was tested as tracer in the in situ experiment but was not included in the laboratory experiment.

6.2 Potential use of solvent extraction technique for enrichment of Fluorescein and Fluorescein derivative

6.2.1 Introduction

A common problem in tracer experiments is that a high dilution is obtained from the injection point to the sampling point. It is therefore important that the dynamic range, i.e., the detection limit concentration divided by the highest possible injection concentration, for a tracer is high enough to be able to study a dilution process.

A tracer used in a wide range of hydrological application is the fluorescent dye tracer Fluorescein (Uranine). It is reported to have good resistance towards adsorption and by using spectrofluorometry it can be measured in concentrations >0.01 μg/l (e.g., Smart and Laidlaw 1977). The Fluorescein derivatives Eosin Y, Eosin B, Phloxine B and Rose Bengal were tested by Albelin et al (1987) in a laboratory test and the results was satisfying. They were therefore used in several *in situ* tracer experiments in the Stripa mine and it is indicated that Fluorescein derivative generally are good non-sorbing tracers.

However, in the first part of the *in situ* experiment in this study (cf. Chapter 4.3) non-satisfying results were found when using the Fluorescein derivatives Phloxine B and Rose Bengal. A possible explanation is that the higher salinity in the Äspö groundwater compared to Stripa in combination with the high concentration used might have caused problem. In the second part of the *in situ* experiment in this study (cf. Chapter 5) two additional Fluorescein derivatives were tested, Eosin Y and Dimethylfluorescein, with satisfying results.

Several other fluorescent derivatives are commercially available (e.g., Dibromofluorescein, Diiodofluorescein, Dinitrofluorescein, Tetrachlorofluorescein and Carboxyfluorescein). A promising tracer application would be the simultaneous use of some of the tracers, an enrichment of these tracers followed by a HPLC/spectrofluorometry measurement of the tracers.

A drawback with both the spectrofluorometry method and the HPLC/spectrofluorometry method is that only a very small part of the sampled solution is used in the detection process. A pre-measuring enrichment technique would therefore make it possible to quantify lower concentrations of Fluorescein in the sampled water and thus increase the dynamic range for the tracer. Furthermore, the spectrofluorometric measurements of Fluorescein are often interfered by naturally occurring fluorescent substances, e.g., humic acids. If the fluorescent dye tracers could be selectively separated, the problem with interfering substances could be decreased.

There are some descriptions of tracer enrichment techniques in the literature. A solid phase extraction technique applied for Fluorescein has been described by Franke et al 1997. In work by Laane et al (1984) and by Hofstraat et al (1991), descriptions solid phase extractions were used for enrichment of Rhodamine WT dye tracer.

A widely used technique for enrichment purposes is the solvent extraction technique in which the distribution of a tracer between an aqueous phase and organic phase is used. By adjusting the chemical conditions of the aqueous phase, the tracer can be selectively extracted to the organic phase. If the conditions are adjusted in an appropriate way, the solubility of the tracer can be much higher in the organic phase compared to the aqueous phase. A large volume of the aqueous phase could thus be contacted with a small volume of an organic phase; when the tracer is transferred to the organic phase, a volumetric enrichment is obtained. This enrichment could also be combined with a strip, i.e., the organic phase containing the tracer is contacted with a new water phase where the conditions have been set favourable for a back-extraction of the tracer. In favourable cases, a smaller water phase can be used in the back extraction and a volumetric enrichment is thus also obtained in the strip step.

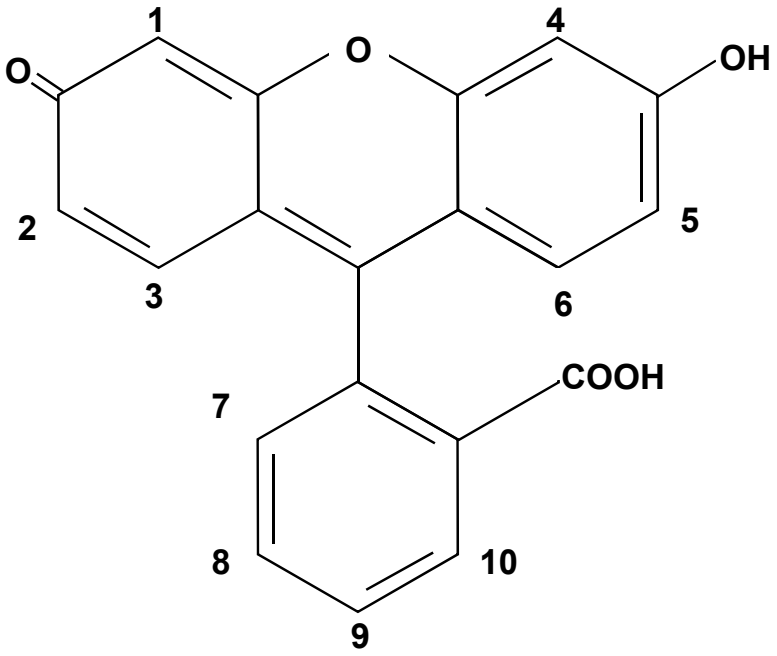
6.2.2 Chemical properties of Fluorescein and its derivative

Fluorescein is protonated according to the scheme given in Figure 6-2. According to the data given by Zanke and Peter (1958) Fluorescein exists as a divalent anion at pH>7, monovalent anion at 7<pH<5, neutral molecule 5<pH<2 and as a monovalent cation at pH<2. Two different forms (isomers) of the neutral molecule are known (cf. Figure 6-2). Different derivatives to Fluorescein are known (examples in Table 6-1) in which different atoms/molecules have been attached to Fluorescein. No data for the protonation constants of these derivatives have been found in literature.

By using solvent extraction technique, only the neutral molecule of Fluorescein can be extracted to an organic phase. However, non-charged form of Fluorescein will still have a considerable polarity and it can be suspected that an organic solvent with some polarity is needed for the extraction of Fluorescein.

Based on the chemistry discussed above, the following potential separation/enrichment scheme was outlined:

1. Addition of HCl to the sampled groundwater in order to decrease the pH to a value where the neutral form of Fluorescein dominates.
2. Extraction to an organic solvent. The choice of the organic phase became an optimisation problem. The extraction of Fluorescein is favoured by a high polarity of the organic phase. However, higher polarity also causes higher solubility of the organic phase in the water phase. For tracer enrichment purposes, it is likely that a comparatively small volume of the organic phase has to be used. Using a too polar organic solvent, the organic phase might therefore be totally dissolved in the water phase. It was decided to try with hexanol since it has high polarity but also comparatively low solubility in the water phase. Alcohols with lower molecular weight (e.g., butanol) would give higher polarity but the higher solubility of that alcohol would have given losses of the organic phase in the water phase, as described above.
3. Back-extraction should be performed by contacting the butanol with an alkaline solution, i.e., the pH should be raised to favour the divalent anion of Fluorescein which would be transferred to the aqueous phase.



	substitution in position #									
Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fluorescein	-	-	-	-	-	-	-	-	-	-
Eosin B	Br	NO_2	-	Br	NO_2	-	-	-	-	-
Eosin Y	Br	Br	-	Br	Br	-	-	-	-	-
Phloxine B	Br	Br	-	Br	Br	-	Cl	Cl	Cl	Cl
Rose Bengal	I	I	-	I	I	-	Cl	Cl	Cl	Cl
Dibromofluorescein	Br	-	-	Br	-	-	-	-	-	-
Diiodofluorescein[1)]	←------- I -------->			←------- I -------->			-	-	-	-
Dinitrofluorescein	NO_2	-	-	NO_2	-	-	-	-	-	-
Carboxyfluorescein[2)]	-	-	-	-	-	-	-	-	←COOH→	
Tetrachlorofluorescein	-	-	-	-	-	-	Cl	Cl	Cl	Cl

1) One Iodine atom is positioned on either position 1, 2 or 3 and another iodine atom is positioned on either position 4, 5 or 6

2) One carboxy group is positioned on either position 9 or 10

Figure 6-1: *Chemical structures of Fluorescein and some Fluorescein derivative.*

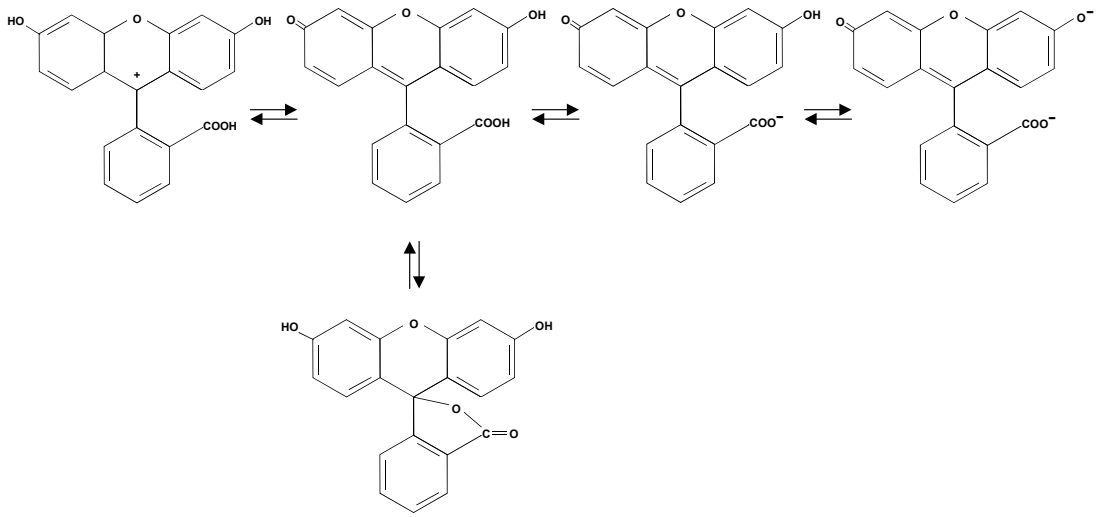


Figure 6-2: *Different protonated forms of Fluorescein.*

6.2.3 Experimental

Extraction

Five samples consisting of 100ml 1M NaCl/0.003M HCl were prepared. A fluorescent dye tracer (Fluorescein, Eosin B, Eosin Y, Phloxine B and Rose Bengal) was added to each solution to give a concentration of 1μM. A sample consisting of Äspö groundwater from the TRUE1 STT1b-experiment (Winberg et al. 2000) was also used. The major component of this water is 0.08M NaCl and 0.03M $CaCl_2$ (a detailed water composition is given by Säfvestad and Nilsson 1999) and it contained a Fluorescein concentration of 0.8μM (Fluorescein, i.e., Uranine, was used as tracer in the experiment). This sample was adjusted to an acidity comparable to the other samples, i.e., 0.003M. 1 ml was sampled from each mixture before the extraction process.

5ml of hexanol were added and the different mixtures were shaken thoroughly for 1 minute. After centrifugation (3000 rpm, 5min), 1ml from the aqueous phase and 1ml from the organic phases were sampled.

Before the spectrophotometric measurements of the samples, addition of NaOH was performed in order to make sure that the strongly fluorescent divalent anion form of the tracers dominated in the solutions. To the water phases, 10μl of 10M NaOH were added to each 1ml sample to obtain a concentration of 0.1M NaOH. To the organic phases, butanol pre-equilibrated with 10M NaOH was added until a strong increase of the colour of the solutions could be visually observed. This was achieved within 5-10μl.

The absorbance of the different samples was measured using a Perkin-Elmer Lambda 19 spectrophotometer (Perkin Elmer, Germany). 1cm cells were used and blanks were registered using 1M NaCl (aqueous phases) and hexanol (organic phases). Absorbance was registered in the visual region (400-600nm).

Examples of the results are given in Figure 6-3 and 6-4. A strong peak (originating from the absorbance of the tracer) is observed in all samples taken before the extraction. Some absorbance can be seen in the samples taken after the extraction, however with a completely different shape than for the tracers. This slight increase of the absorbance is indicative of turbidity, probably caused by a small emulsion of traces of the organic phase remaining in the water phase. No indication of a peak can be seen in any of the samples taken after the extraction, showing that the tracers are extracted quantitatively. In Figure 6-3 b) and 6-4 b) strong absorbance are observed in the measurements of the organic phases, more than one order of magnitude higher absorbance than the absorbance in the samples taken from the water phase before the extraction. However, this absorbance ratio can not be used for quantification, since different solvents are used. The shapes are similar as for the measurements of the aqueous phases before the extraction; however, a spectrophotometric shift towards longer wavelengths can be observed. The measurements of the organic phases show that a significant mass transfer has occurred from the aqueous phase to the organic phase.

The results of the extraction are expressed as D-values, i.e., the ratio of the tracer concentration in the organic phase divided by the concentration of the tracer in the water phase. Based on the absorbance measurements before and after the extraction, the D-value can be calculated according to:

$$D = \frac{A_{pre-ex} - A_{post-ex}}{A_{post-ex}}$$

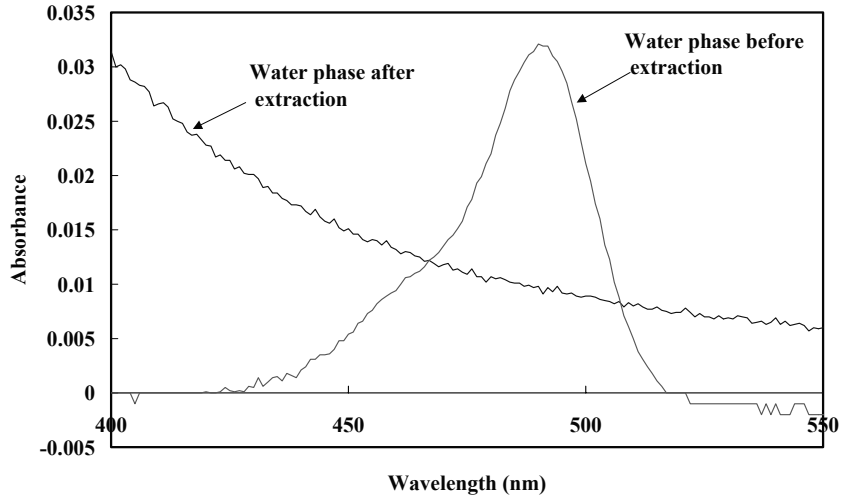
where $A_{\text{pre-ex}}$ is the absorbance measured before the extraction and $A_{\text{post-ex}}$ is the absorbance measured after the extraction. However, since no tracer peak could be identified in the samples after the extraction, the following approach was used in order to estimate the minimum D-values for the present system:

- The average of the absorbance at the 10 wavelengths with highest absorbance in the samples taken before the extraction, was used as the $A_{\text{pre-ex}}$
- The doubled standard deviation of the absorbance (at the same wavelengths) in the samples taken after the extraction, was used as the $A_{\text{pre-ex}}$

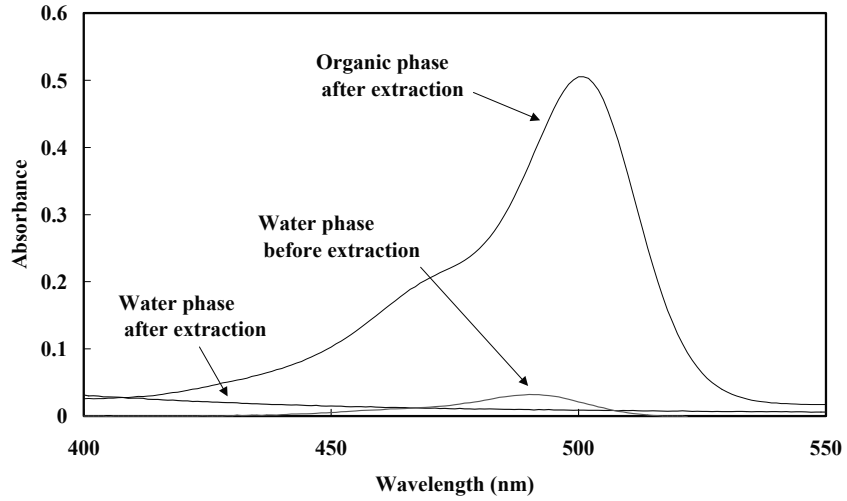
The results (Table 6-2) show that the concentrations in the organic phases are at least 50-100 times higher in the organic phase than in the aqueous phase. It is indicated that a volume ratio of 5ml hexanol to 100 ml water can extract the fluorescent dye tracers completely, i.e., a volumetric enrichment of a factor ~20 is demonstrated by the extraction step.

Table 6-2 Results of the extraction of Fluorescein and Fluorescein derivative from aqueous to hexanol

	Fluorescein (NaCl)	Fluorescein (Äspö GW)	Eosin B (NaCl)	Eosin Y (NaCl)	Phloxine B □□□□□□ □□□□□□	Rose Bengal (NaCl)
D (5ml org/ 100 ml aq)	>40	>40	>90	>120	>80	>70
D (65ml org/ 9ml aq)	>650	-	>3300	-	-	-

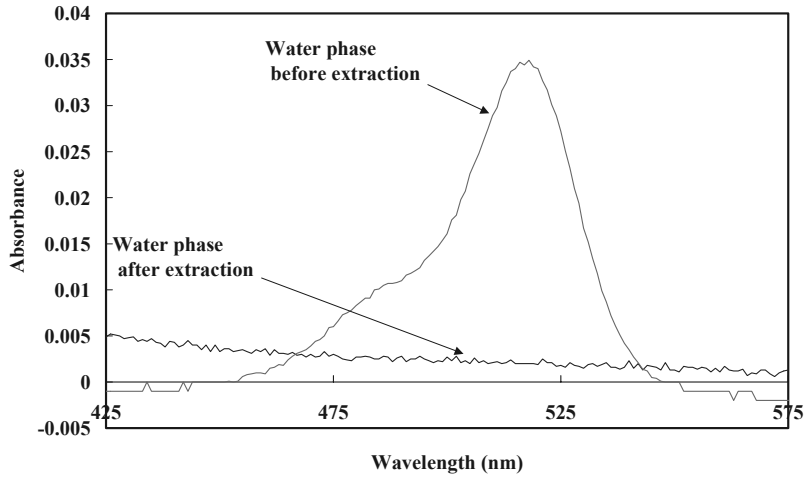


a)

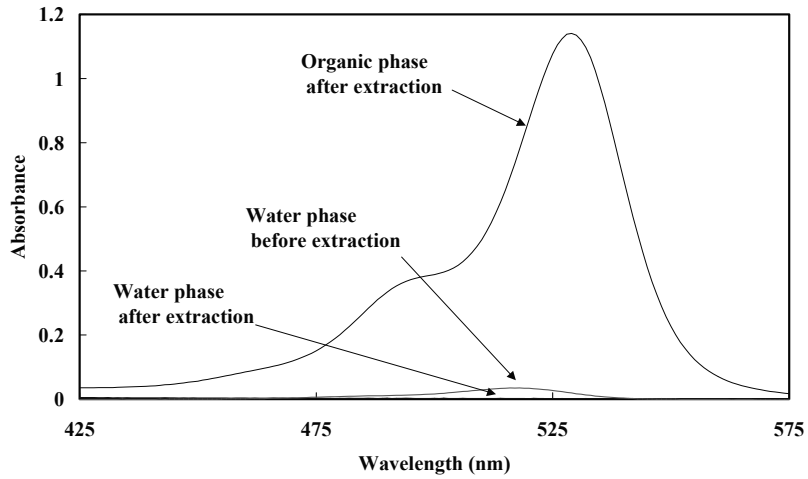


b)

Figure 6-3: *Absorbance measured from the extraction studies samples. Fluorescein was used as tracer (1μM) and extraction was performed using 100ml water phase and 5ml organic phase. The chart below is an expansion of the chart above, to highlight the low absorbance measured in the water phases.*



a)



b)

Figure 6-4: *Absorbance measured from the extraction studies samples. Eosin B was used as tracer (1μM) and extraction was performed using 100ml water phase and 5ml organic phase. The chart below is an expansion of the chart above, highlighting the low absorbance measured in the water phases.*

Back-extraction (strip)

In the back-extraction studies, a loading of tracer into the organic phase was first performed. Two batches of 65ml hexanol were shaken with two 10ml solution consisting of 1M NaCl/0.003M HCl. In the first batch, 10μM of Fluorescein was added to the water phase and in the other batch 10μM of Eosin B was added. 1 ml of the different water phases was sampled before the extraction was performed. The mixtures were shaken for 1min and the phases were allowed to separate without centrifugation. 1ml of the water phase was sampled and thereafter 10 ml of the hexanol was sampled. The hexanol was transferred to a new vial and 1 ml of 0.1M NaOH was added. The new mixtures were shaken for 1min, a small (<1ml) amount of the water phase was sampled and was centrifuged in 3000rpm for 5min. 0.25 ml was sampled from this centrifuged sample and mixed with 0.75ml 1M NaOH. The same procedure was performed with the samples taken before and after the first extraction step.

The absorbance of the different samples was measured according to the procedure mentioned above. Similar to the first extraction process, no concentrations of the tracers remained in the water phase after the loading process. The minimum D-values were evaluated as described above and were found to be at least one order of magnitude higher than in the previous extraction, results are given in Table 6-2.

The results from the back-extraction were evaluated by comparing the maximum absorbance from the samples taken before the extraction and the samples taken after the strip (compensated by the volume ratios, illustrated in Figure 6-5 and 6-6). For Fluorescein, it was found that the absorbance of the strip solution were higher than for the solution sampled before injection, indicating that ~110 percent of the tracer was back-extracted which is difficult to explain. However, the water solubility in hexanol combined with the hexanol solubility in water, 7 and 0.7 weight%, respectively, reported by Rydberg et al. (1992), may have caused that the volume compensations are incorrect. In any case, it is indicated that the back-extraction is almost complete and that a volumetric enrichment of Fluorescein by a factor 10 can be obtained in the stripping step.

For Eosin B it is found that only 50% of the tracer is back-extracted. However, since a volume ratio of 1/10 is used, it is demonstrated that a volumetric enrichment of a factor 5 is possible to obtain for Eosin B in the stripping step.

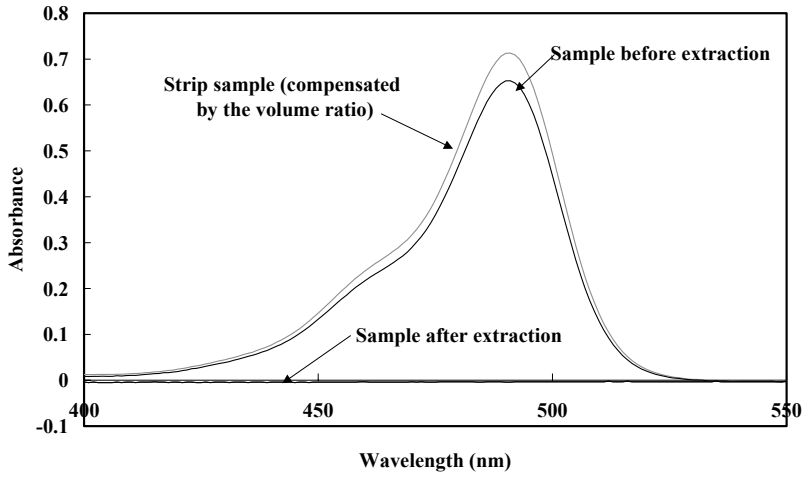


Figure 6-5: *Absorbance measured from the extraction and back-extraction samples. Fluorescein was used as tracer (10μM) and extraction was performed using 9ml water phase and 65ml organic phase .In the back-extraction step, 10 ml of the organic phase was contacted with 1ml of 0.1M NaOH.*

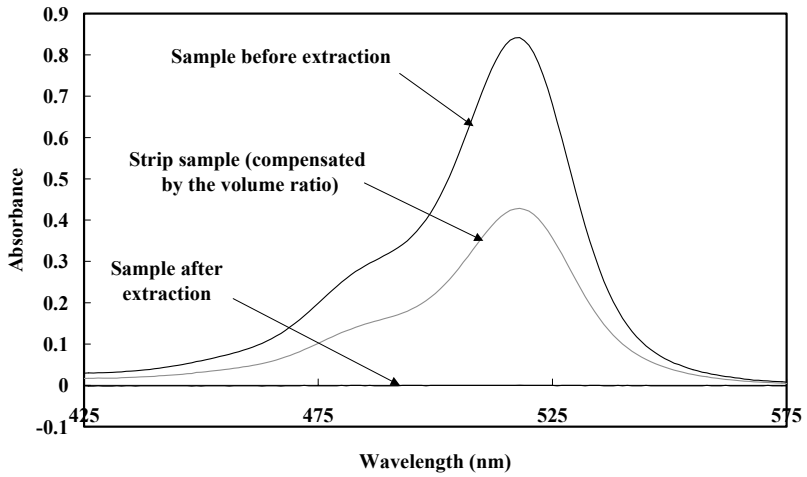


Figure 6-6: *Absorbance measured from the extraction and back-extraction samples. Eosin B was used as tracer (10μM) and extraction was performed using 9ml water phase and 65ml organic phase. In the back-extraction step, 10 ml of the organic phase was contacted with 1ml of 0.1M NaOH.*

6.2.4 General Conclusions and future perspectives

The results of the present work indicate that solvent extraction of Fluorescein and Fluorescein derivatives is a promising technique. The minimum D-values obtained show that a significant volumetric enrichment by is obtained by an extraction of the tracers to a hexanol phase. A good back-extraction is observed for Fluorescein; however, the back-extraction of Eosin B seems to bee more complex. Combining the minimum enrichment obtained for Fluorescein in the extraction step and in the strip step, an enrichment of a factor 400 is indicated. A procedure for treating samples with this method on laboratory could easily be outlined.

An interesting future perspective of this method would be to construct an automated system to be used *in situ*. Large volume of effluent water should be treated with this enrichment method that would make it possible to perform tracer experiment with very large dilution factors. One possibility would be to design an on-line automated separation system, e.g., a mixer-settler system (e.g., Rydberg et al. 1992), based on the present method.

The solvent extraction studies indicate that it is applicable to all the Fluorescein derivatives used in the investigation. It should be emphasised that several other Fluorescence derivative exists which are likely to be possible to extract with the present method.

Some potential limitations of the method should be mentioned. The experiments in this work have been one using mostly non-natural waters without any impurities. Furthermore, comparable high concentrations (1-10μM) have been used, measured using absorbance spectrophotometry. In applications aimed for enrichment before spectrofluorometric measurements, concentrations <6 orders of magnitude lower may occur. It is also possible that natural fluorescent substances (e.g., humic acids) could be extracted and enriched by the method as well. It is also possible that the hexanol contains fluorescent impurities which may be enriched in the strip solution and therefore interfere in the spectrofluorometric measurements.

For the back extraction step, it must be emphasised that a small part of the water phase is dissolved in the hexanol. When applying the extraction process on a natural groundwater with a high concentration of Ca^{2+}, it is likely that problem with precipitations of Ca(OH)2 and/or $CaCO_3$ can occur when the organic phase is contacted with the highly alkaline strip solution. This formation of precipitation can probably be prevented by adding a small amount of a strong complexing agent (e.g., EDTA or DTPA) to the strip solution.

7 Discussion and conclusions

7.1.1 Tracer evaluation

Helium:

- He tracer tests are feasible to perform at the Äspö HRL. The He tracer technique is applicable at the True Block Scale Experiment site.
- Using He as tracer requires a relatively small effort to exclude or quantify experimental artefacts.
- It is most likely that the comparison of He with other non-reactive tracers can demonstrate the effect of matrix diffusion as a retention process.
- ^{4}He measurements in the groundwater at the test site showed a 2 to 3 order of magnitude increased concentration compared to surface waters. Depressurising (from 30 to 0 bar) of the groundwater caused no gas bubbles in the outflow line, which could have biased the on-line detection.

Fluorescent dyes:

- Sampling and use of HPLC tracer analysis technique work well. Therefore, it is possible to run tracer tests with a large number of fluorescent tracers.
- Sulforhodamine G, Phloxine and Rose Bengal all showed a non-conservative behaviour. All other tracers are possible candidates for future tracer experiments.
- On-line detection of Uranine by the fibre optic fluorometer worked well and allowed to monitor the tracer input function and the breakthrough curve at the extraction site.
- A new method for enrichment of Fluorescein (Uranine) and Fluorescein derivatives by solvent extraction has been developed and shown to work well. An enrichment factor of at least 400 was obtained.

Metal-complexes:

- The sampling technique as well as the high resolution ICP-MS analysis technique works well. The analysis technique makes it possible to analyse a large number of metal-complexes at the same time.
- The complex Ni-EDTA suffered irreversible losses and are not to be regarded as non-reactive. All other metal-complexes are to be regarded as possible candidates for future tracer tests. Additional metal-complexes for possible use in future tracer tests can be identified from earlier experiments performed at Finnsjön (Andersson et. al, 1993; Gustafsson and Nordqvist, 1993) and Stripa (Olsson (*ed)*, 1992). The metal-complexes in question are DTPA (Dy, Eu and Tb) and Tm-EDTA.
- Perrhenat (ReO_4^-) also showed a conservative behaviour and is therefore a possible tracer candidate in future tracer experiments.

Benzoates:

- In contrast to the literature the benzoic acids proved difficult go get in to aqueous solution. It was possible to solve approximately 10 g/l if NaOH was added to the solution. The amount of NaOH added was equal to the ionic strength of the benzoic acid in question. This concentration is however not enough to ensure successful detection of the entire breakthrough curve with the detection levels given by the approached commercial laboratories. Another deterrent fact is that the injection of a tracer solution of 10 000 ppm would be very costly.

- The detection level for the HPLC tracer analysis technique was, according to the commercial analysis laboratories that were asked to perform the analysis, considerably higher than the levels given in the literature. A new analysis technique was therefore developed. The presented method of LC-MS-MS (Liquid Chromatography double Mass Spectrometry) detection has shown to be able to measure the fluorinated benzoic acids reliable >0.1µg/l. Furthermore, it has been shown that by using the method all the five added fluorinated benzoic acids can be measured simultaneously and without any mutual interference.

- The results of the in-situ experiments with benzoic acids indicate that the mass recovery is lower (26-56%) than what could be expected from a conservative tracer. However, peak travel times are similar to the reference tracer (Uranine) and the tailing is also similar indicating a kinetic process rather than a reactive one. It cannot be ruled out that the long time period between sampling and analysis (more than one year), during the development of the detection method, had an influence on the benzoic acids, e.g. through microbial degradation.

- The somewhat inconclusive results of the tracer tests makes it difficult to judge whether benzoic acids could be used as conservative tracers or not, more field tests are required. However, given the relatively low solubility and high price, benzoic acids are not recommended as a first choice for future tracer tests.

Table 7-1: Dynamic range for the selected non-reactive tracers.

Tracer	Solubility	Detection limit	Background in Äspö water	Dynamic range Solubility/ Detection limit	Total injected mass M(0)
Deuterium	0.99	0.4 ppm	145.8 ppm	$2.5 \cdot 10^{8}$	
Uranine	200 g/l	$2.0 \cdot 10^{-9}$ g/l [4]	$< 1.0 \cdot 10^{-7}$ g/l	$1.0 \cdot 10^{11}$	$4.8 \cdot 10^{-4}$ g [6]
					$1.1 \cdot 10^{-3}$ g [7]
					$2.3 \cdot 10^{-3}$ g [8]
Eosin	200 g/l	$1.0 \cdot 10^{-8}$ g/l [4]	$< 1.0 \cdot 10^{-8}$ g/l	$2 \cdot 10^{10}$	$1.2 \cdot 10^{-3}$ g
Dimethylfluorescein	200 g/l	$6.0 \cdot 10^{-9}$ g/l [4]	$< 1.0 \cdot 10^{-8}$ g/l	$3.3 \cdot 10^{10}$	$8.4 \cdot 10^{-4}$ g
Naphthionate	200 g/l	$5.0 \cdot 10^{-7}$ g/l [4]	$< 5.0 \cdot 10^{-7}$ g/l	$4 \cdot 10^{8}$	$9.6 \cdot 10^{-3}$ g
Pyranine	150 g/l	$1.0 \cdot 10^{-8}$ g/l [4]	$< 1.0 \cdot 10^{-8}$ g/l	$1.5 \cdot 10^{10}$	$9.6 \cdot 10^{-4}$ g
UV1	200 g/l	$1.0 \cdot 10^{-8}$ g/l [4]	$< 1.0 \cdot 10^{-8}$ g/l	$2 \cdot 10^{10}$	$1.2 \cdot 10^{-3}$ g
Helium[1]	0.00842 ccSTP/ml	$8.0 \cdot 10^{-8}$ ccSTP/ml	$< 8.0 \cdot 10^{-8}$ ccSTP/ml	$1.05 \cdot 10^{5}$	
In-EDTA	10 g/l	$1.0 \cdot 10^{-8}$ g/l [5]	$< 1.0 \cdot 10^{-8}$ g/l	$1.0 \cdot 10^{9}$	$2.25 \cdot 10^{-3}$ g
Benzoic Acids[9]	10 g/l	$1.0 \cdot 10^{-7}$ g/l	$<1.0 \cdot 10^{-7}$ g/l	$1 \cdot 10^{8}$	$4\text{-}10 \cdot 10^{-3}$ g

Tracer	Solubility	Detection limit	Background in Äspö water	Dynamic range Solubility/ Detection limit	Total injected mass M(0)
Yb-EDTA	15 g/l	$1.0 \cdot 10^{-8}$ g/l [5)]	< $1.0 \cdot 10^{-8}$ g/l	$1.5 \cdot 10^{9}$	$2.21 \cdot 10^{-3}$ g
Lu-EDTA	15 g/l	$1.0 \cdot 10^{-8}$ g/l [5)]	< $1.0 \cdot 10^{-8}$ g/l	$1.5 \cdot 10^{9}$	$2.09 \cdot 10^{-3}$ g
Tm-EDTA	10 g/l	$5.0 \cdot 10^{-8}$ g/l [5)]	< $5.0 \cdot 10^{-8}$ g/l	$2.0 \cdot 10^{8}$	$1.44 \cdot 10^{-3}$ g
Gd-DTPA	15 g/l	$1.0 \cdot 10^{-8}$ g/l [5)]	< $1.0 \cdot 10^{-8}$ g/l	$1.5 \cdot 10^{9}$	$2.02 \cdot 10^{-3}$ g
Ho-DTPA	15 g/l	$1.0 \cdot 10^{-8}$ g/l [5)]	< $1.0 \cdot 10^{-8}$ g/l	$1.5 \cdot 10^{9}$	$2.38 \cdot 10^{-3}$ g
Dy-DTPA	10 g/l	$1.0 \cdot 10^{-8}$ g/l [2)]	< $1.0 \cdot 10^{-8}$ g/l	$1.0 \cdot 10^{9}$	-
Eu-DTPA[2)]	10 g/l	$1.0 \cdot 10^{-8}$ g/l [2)]	< $1.0 \cdot 10^{-8}$ g/l	$1.0 \cdot 10^{9}$	-
Tb-EDTA[2)]	10 g/l	$1.0 \cdot 10^{-8}$ g/l [2)]	< $1.0 \cdot 10^{-8}$ g/l	$1.0 \cdot 10^{9}$	-
ReO_4^-	10 g/l	$1.0 \cdot 10^{-8}$ g/l	< $1.0 \cdot 10^{-8}$ g/l	$1.0 \cdot 10^{9}$	$1.02 \cdot 10^{-3}$ g
^{82}Br [3)]	10^{9} Bq/l	0.7 Bq/l	< 6.0 Bq/l	$1.4 \cdot 10^{8}$	-
^{131}I [3)]	10^{7} Bq/l	0.5 Bq/l	< 2.0 Bq/l	$2.0 \cdot 10^{8}$	-

1) T: 20° C, Pressure: 1 bar
Detection levels for ICP-MS (SGAB Analytica, Luleå)

2) Approximate detection levels for ICP-MS (SGAB Analytica, Luleå)

3) Maximum used amount, values calculated using a maximum level of 10 ALI.
(Annual Limit of Intake). Approximate levels of detection (TRACER HANDBOOK)

4) HPLC and spectrofluorometry detection limits based on sample analysis for pilot tracer tests

5) Detection levels for LC-MS-MS (Analycen AB, Lidköping)

6) First pilot tracer test

7) Second pilot tracer test, second run

8) Second pilot tracer test, third run

9) 2,3-DFBA, 2,6-DFBA, 3,5-DFBA, 2,3,4,5-TFBA, PFBA

7.1.2 Dynamic range

It is important to stress that the solubility for the dyes given in Table 7-1 are not of any practical use. It is not recommendable to inject solutions of higher concentrations than one tenth of what is given for the dyes in Table 7-1. Solutions of higher concentrations will result in viscosity and density effects during the injection phase. The viscosity and density effects will bias the tracer test. It should also be stressed that the dynamic range, for the dyes and Helium, of any practical use only will be one tenth of that given in Table 7-1.

The detection limit does not only depend on the sensitivity of the detection method and the instrument used but also on the natural background in the water samples. The concept of natural background means not only the background of the compound itself but also of chemicals, bacteria, particles etc. that affects the wavelengths that the compound of interest responds to. A detection limit of practical use is very dependent on the characteristics of the water. The background levels of the metal-complexes and perrhenat are lower that the detection limits of the other compounds. The background levels given in Table 6-1 for the metal-complexes and perrhenat are in general higher than the levels given by Säfvestad and Nilsson (1999). The actual detection levels of the metal-complexes and perrhenat are at least 10 times lower than the levels given in Table 7-1. The reason for the higher detection levels given in Table 7-1 is the fact that the water samples in these experiments had to be diluted. For every dilution of the samples the detection levels increases 10 times. The fact the background level of the dye tracers are higher than the detection limit is result of the natural background and contamination from the flushing water used for drilling.

The detection levels given for the metal-complexes and perrhenat in Table 7-1 concern analysis made with high resolution ICP-MS.

The two radioactive tracers, ^{82}Br and ^{131}I, are included in Table 7-1 as a comparison. These tracers will be used in the final phase of the tracer tests together with radioactive sorbing tracers. The word solubility is not appropriate to use about ^{82}Br and ^{131}I. The use of radioactive tracers is not limited by the solubility. The values given for ^{82}Br and ^{131}I in Table 7-1 are maximum levels that are possible/practical to use with consideration to the safety of the personnel. The levels are calculated from a maximum level of 10 ALI (Annual Level of Intake). The detection limits in Table 7-1 for ^{82}Br and ^{131}I are for twelve hour measurements.

References

Albelin, H., Birgersson, L., Gidlund, J., 1987: 3-D Migration experiment – Report 2: Instrumentation and Tracers, SKB Stripa Report 87-20

Andersson P, Nordqvist R, Persson T, Eriksson C-O, Gustafsson E, Ittner T, 1993: Dipol tracer experiment in low-angle fracture zone at Finnsjön – Results and interpretation. The fracture Zone Project – Phase 3. Swedish Nuclear Fuel and Waste Management Company. Technical Report TR 93-26.

Andersson P, 1995: Compilation of tracer tests in fractured rock. Swedish Nuclear Fuel and Waste Management Company. Progress Report PR 25-95-05.

Andersson P, 1996: TRUE 1st stage programme. Experimental data and preliminary evaluation of the TRUE-1 radially converging tracer test (RC-1). Swedish Nuclear Fuel and Waste Management Company. Äspö Hard rock Laboratory Progress report HRL-97-24.

Benson C, Bowman R, 1994: Tri- and tetraflourobensoates as nonreactive tracers in soil and groundwater. Soil Sci. Soc. Am. J. 58: 1123-1129.

Birgersson, L., Widén, H., Ågren, T., Neretnieks, I., Moreno, L., 1992: Site characterization an validation – Tracer migration experiment in the validation drift, Report 2, Part1: Performed experiments, results and evaluation, SKB Stripa Project Technical Report 92-03

Björkeström L, 1993: Monosfäriska plastpartiklar som spårämnen. Master thesis, Dep. of Nuclear Chemistry, Chalmers University of Technology, pp 75.

Bowman R, Gibbens J, 1992: Difluorobenzoates as nonreactive tracers in soil and ground water. Ground Water. 30: 8-14.

Byegård J, Skålberg M, 1992: Tracer handbook. Swedish Nuclear Fuel and Waste Management Company. Äspö Hard rock Laboratory Progress report 25-92-11.

Byegård J, 1995: Developments of some In Situ tracer techniques applied in groundwater research. Dr. thesis, Chalmers University of Technology, pp 58

Eikenberg J, Frick U, Fierz T, Bühler Ch, 1992: On-line detection of stable helium isotopes in migration experiments, Tracer Hydrogeology, Hötzl and Werner(eds.) 1992 Balkema, Rotterdam, ISBN 9054100842

Franke, C., Westerholm, H., Niessner, R., 1997: Solid-Phase Extraction (SPE) of the fluorescence tracers Uranine and Sulforhodamine B, Wat. Res. 31, 2633-2637

Frick U, Alexander W R, Bayens B, Bossart O, Bradbury M H, Bühler C, Eikenberg J, Fierz T, Heer W, McKinley I, Smith P, 1992: Grimsel Test Site: The radionuclide migration experiment, overview of investigations 1985 – 1990. Nagra Technical Report 91-04, Wettingen Switzerland

Gustafsson E, Nordqvist R, 1993: Radially Converging Tracer Test in a Low-Angle Fracture Zone at the Finnsjön site, Central Sweden: the Fracture Zone Project – Phase 3. SKB Technical Report. TR 93-25. Swedish Nuclear Fuel and Waste Management Company. Stockholm.

Hoofstraat, J., W., Steendijk, M., Vriezekolk, G., Schreurs, W., Broer, G., Wijnstok, N., 1991: Determination of Rhodamine WT in surface water by solid-phase extraction and HPLC with fluorescence detection, Wat. Res. 25, 883-890

Jones T, Kelley V, Pickens J, Upton D, Beauheim R, Davies P, 1992: Integration of interpretation results of tracer tests performed in the Culebra dolomite at the Waste isolation pilot plant site. SAND92-1579. Albuquerque, NM: Sandia National Laboratories.

Käss W, 1998: Tracing technique in geohydrology. Balkema, 581 pp.

Laane, R, Manuels, M, Staal, W., 1984: A procedure for enriching and cleaning up Rhodamine B and Rhodamine WT in natural waters, using a SEP-PAK C18 cartridge, Wat. Res. 18, 163-165

McCarville M E, Bergin J, Hampton D R, 1995: Tracers for immiscible hydrocarbons in groundwater: laboratory experiments. IAHS Publ. no. 229

Olsson O (ed), 1992: Site characterisation and validation – Final report. Stripa Project TR 92-22. Swedish Nuclear Fuel and Waste Management Company. Stockholm.

Ozima M, Podosek F A, 1983: Noble gas geochemistry. Cambridge University Press, England

Ptacek C J, Gillham R W, 1992: Laboratory and field measurements of non-equilibrium transport in the Borden aquifer, Ontario, Canada. J. Contam. Hydrol., 10: 119-158.

Rich, R. A., Holland, H. D. and Petersen, U., 1977: Hydroterminal uranium deposits. Developments in economic geology. Elsevier Scientific publishing Company, Amsterdam, 264 pp.

Rydberg, J., Musikas, C., Choppin, G., 1992: Principles and practices of solvent extraction, Marcel Dekker, New York.

Smart P L, Laidlaw I M S, 1977: An evaluation of some dyes for water tracing. Water Resour. Res. 13(1), 15-33.

Stetzenbach K, Farnham I, 1994: Organic anionic tracers: Chemistry and toxicity. Proceedings from the second tracer workshop. Univ. of Texas at Austin, Nov. 14-15, pp 23-32.

Säfvestad A, Nilsson A-C, 1999: Compilation of groundwater chemistry data January 1995 to April 1998. Swedish Nuclear Fuel and Waste Management Company. Äspö Hard Rock Laboratory International Progress Report IPR 99-13.

Winberg A (ed), 1996: First TRUE Stage – Tracer Retention Understanding Experiments. Descriptive structural – hydraulic models on block and detailed scales of the TRUE-1 site. Swedish Nuclear Fuel and Waste Management Company. Äspö Hard Rock Laboratory International Cooperation Report ICR 96-04.

Winberg A, Andersson P, Hermanson J, Byegård J, Cvetkovic V and Birgersson L, 2000: Final report of the first stage of the tracer retention understanding experiments. SKB Technical report TR-00-07.

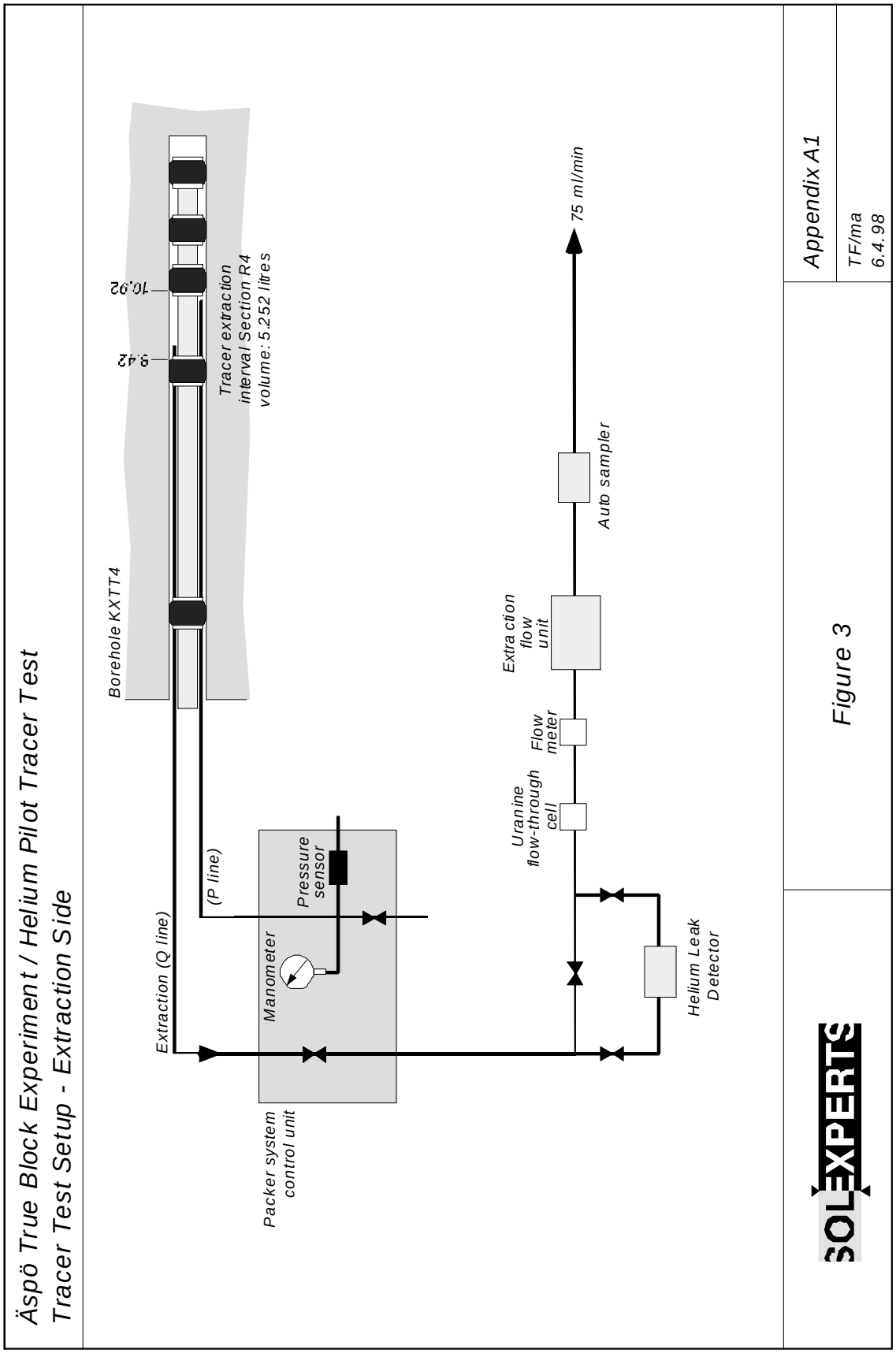
Wilson J L, Linderfelt W R, 1994: Field tracer experiment design problems at the Borden Site. Proceedings from the second tracer workshop. Univ. of Texas at Austin, Nov. 14-15, pp 11-22.

Zanke, V., Peter, W, 1958: (in german) the prototropic forms of fluorescein, Chem. Beer. 91, 572-580

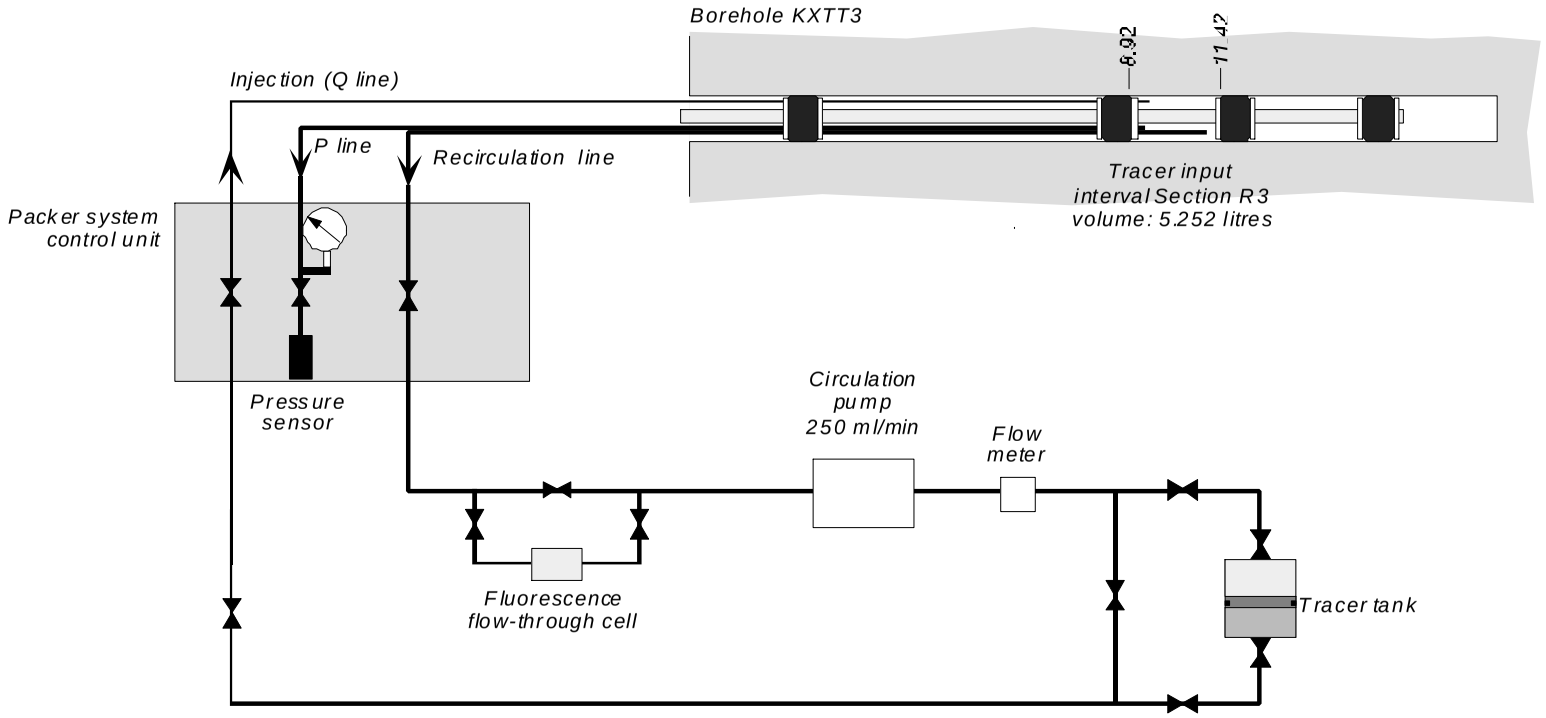
Appendices

Appendix 1:	Figures of the experimental set-up for the tests including Helium
Appendix 2:	Tracer injection and breakthrough curves for the second Pilot tracer test run #1
Appendix 3:	Tracer injection and breakthrough curves for the second Pilot tracer test run #2
Appendix 4:	Development of a LC-MS-MS method for measurement of fluorinated benzoic acids

Appendix 1


Äspö True Block Experiment / Helium Pilot Tracer Test
Tracer Test Setup - Extraction Side
Borehole KXTT4
10.92
9.42
Tracer extraction interval Section R4
volume: 5.252 litres
Extraction (Q line)
(P line)
Pressure sensor
Manometer
Packer system control unit
Uranine flow-through cell
Flow meter
Extraction flow unit
Auto sampler
75 ml/min
Helium Leak Detector
Figure 3
SOLEXPERTS
Appendix A1
TF/ma
6.4.98

Äspö True Block Experiment / Helium Pilot Tracer Test
Tracer Test Setup - Injection Side



SOLEXPERTS

Figure 2

Appendix A1

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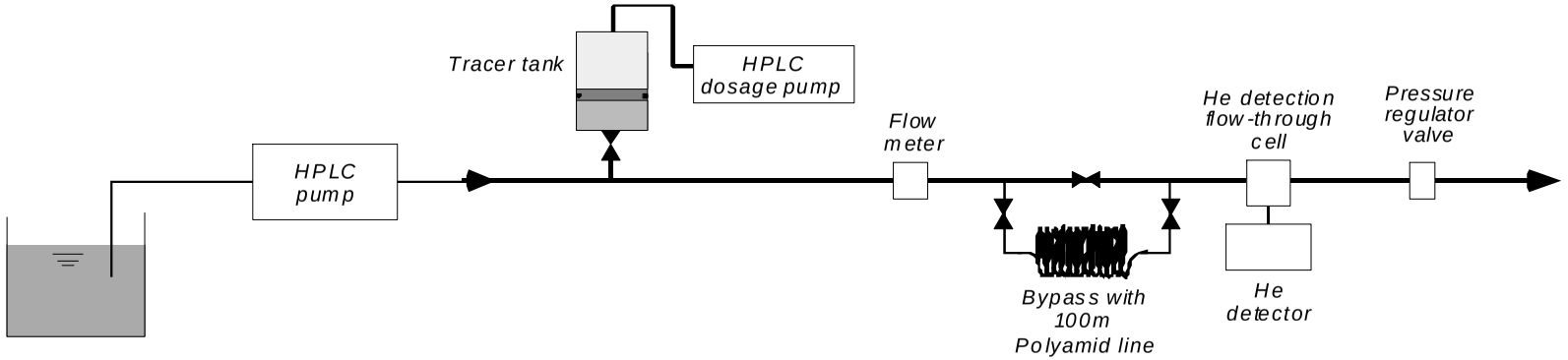
Äspö True Block Experiment / Helium Pilot Tracer Test
Laboratory Tests



SOLEXPERTS

Figure 1

Appendix A1

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Appendix 2

Log Book: Tracer test 1

Log book:	**Tracer Test 1**

I. General Setup:	Injection borehole:	KXPP3-Interval R3	
	Extraction borehole:	KXPP4-Interval R4	
	Injection flow rate:	10 ml/min	
	Extraction flow rate:	75 ml/	
	Tracer used:	He3, Uranine (SOLEXPERTS online measurements); other tracers are sampled by Geosigma	
	Tracer input:	Tracer cocktail # 2	
	Concentration in tank:	He-3:	3.38 E-05 mbar l/sec
		Uranine	8 ppm (44.7 V)
	Tracer tank volume:	2500 ml	
	Interval volume:	5.2 l	
	Data files: tr-test1	Start 3.3.99	

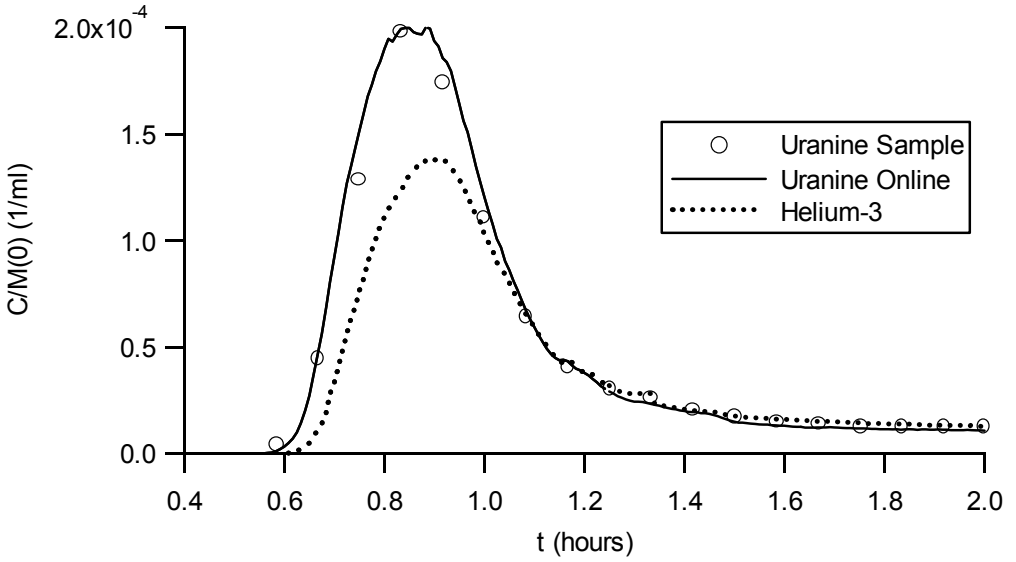
II. Test Schedule:			
date	time	activity	comments
02.03.99	13 to 17:30	Transportation and installation of the equipment	
		Laser of the fibre optic fluorometer did not start up, because of the humidity	
03.03.99	8:30 to 10	Preparing the test setup and calibration setup	
	10 to 11	Start calibration of the He-3 tracer at the extraction side (tracer 75 times diluted)	
		He-3: 4.5 E-07 mbar l/kPa	Calibration file: pretr1.dat
	11 to 12	Transport of the fibre optic fluorometer to the workshop:	
		Laser works fine under less humid conditions	
	13 to 14	Calibration the Uranine injection concentration with the fibre optic fluorometer	
		Uranine: 44.7 V = 8 ppm	Calibration file: pretr2.dat
	14 to 15	Final installation of the injection setup	
	15:00:48	Start tracer injection: Circulation at 250 ml/min	(15:00:00 "GEOSIGMA" time)
	15:05:30	First appearance of tracer Uranine at the injection fluorescence flow through cell	
	15:06:00	Tracer injection tank closed	
	15:06:50	Fluid exchange bypass opened	
	15:28	First arrival of Uranine at the extraction site	
	15:29	First arrival of He-3 at the extraction site	
	15:43	First Uranine peak at the extraction site	
	15:47	Second Uranine peak and He-3 peak at the extraction site	
	15:58	Fluid exchange bypass closed	
03.04.99	09:23	Stop injection, extraction continues	
	09:26	End of data file	
	9:30 to 10	Calibration of Uranine at the extraction side	Calibration file: pretr3.dat
		18.7 V = 10.6 ppb	

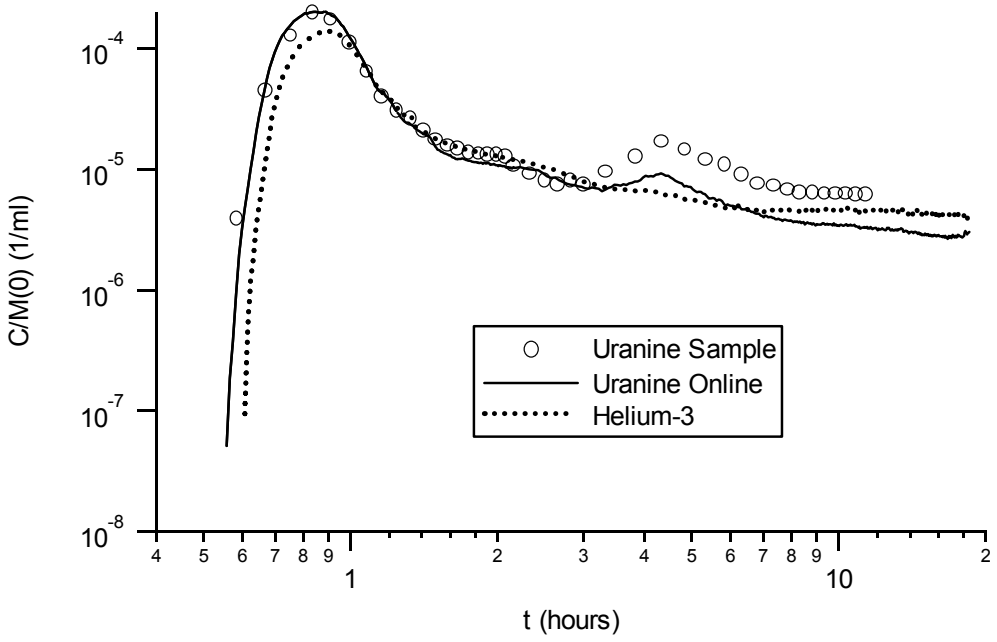
Plots: Tracer test 1

- Tracer input, linear and logarithmic scale
- Breakthrough of Uranine and Helium, linear and logarithmic scale
- Breakthrough of Uranine and Eosin, linear and logarithmic scale
- Breakthrough of Uranine and Sulpho Rhodamine G, linear and logarithmic scale
- Breakthrough of Uranine and Pyranine, linear and logarithmic
- Breakthrough of Uranine and Naphthionate, linear and logarithmic scale
- Breakthrough of Uranine and UV1, linear and logarithmic scale
- Breakthrough of Uranine and Dimethylfluorescein, linear and logarithmic scale
- Breakthrough of Uranine and Deuterium, linear and logarithmic scale

Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

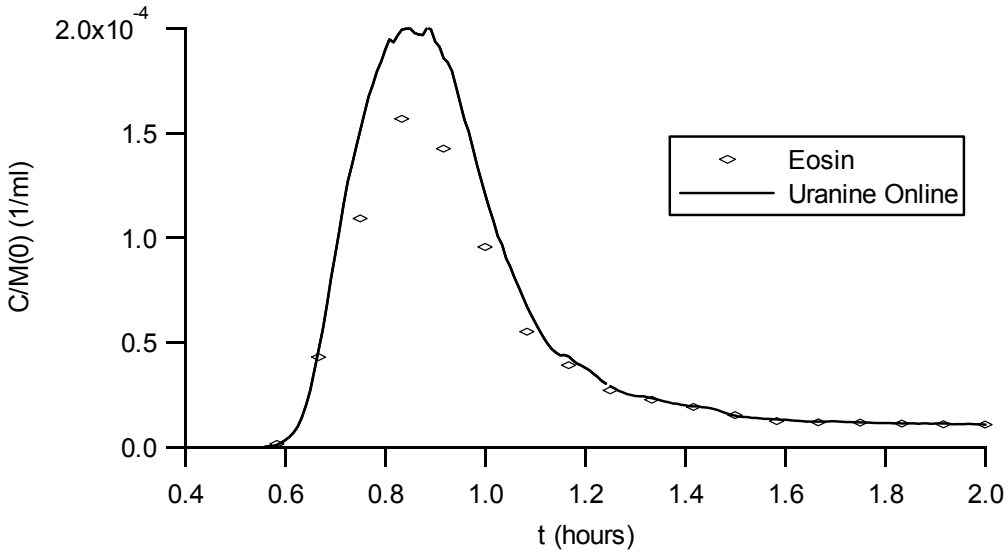
Breakthrough of Uranine (online and sample) and Helium, linear and logarithmic scale

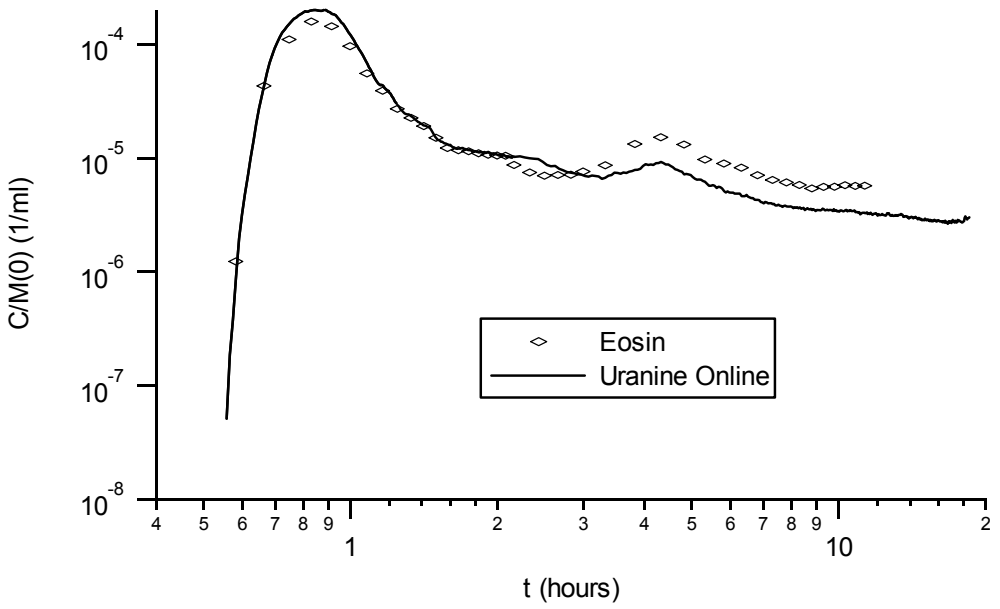




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

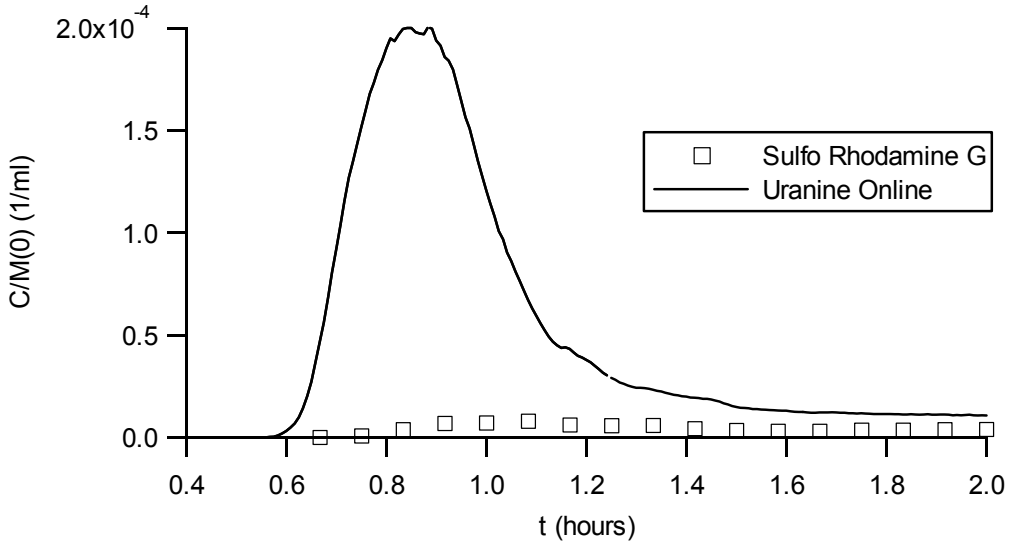
Breakthrough of Uranine and Eosin, linear and logarithmic scale

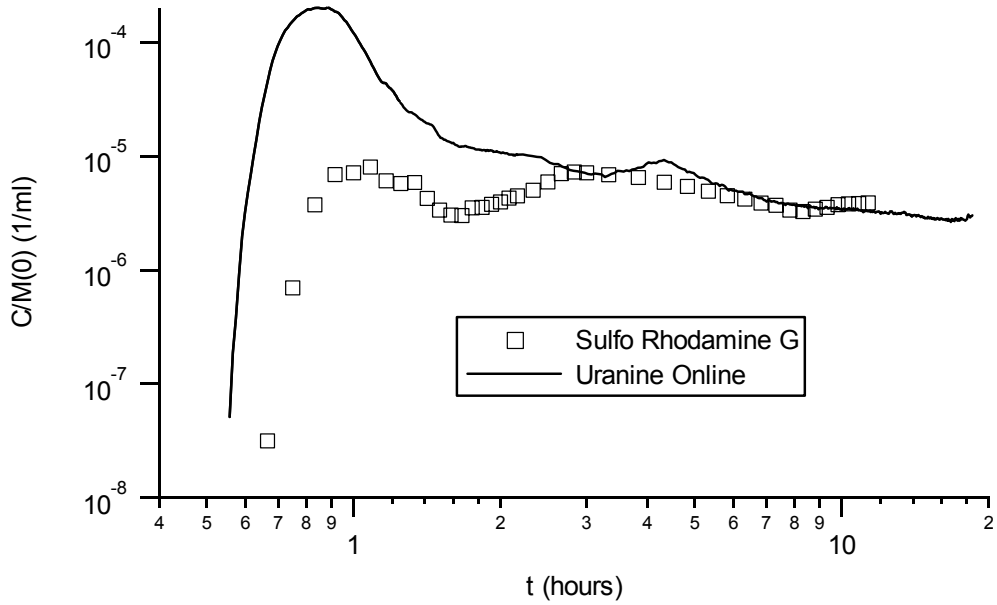




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

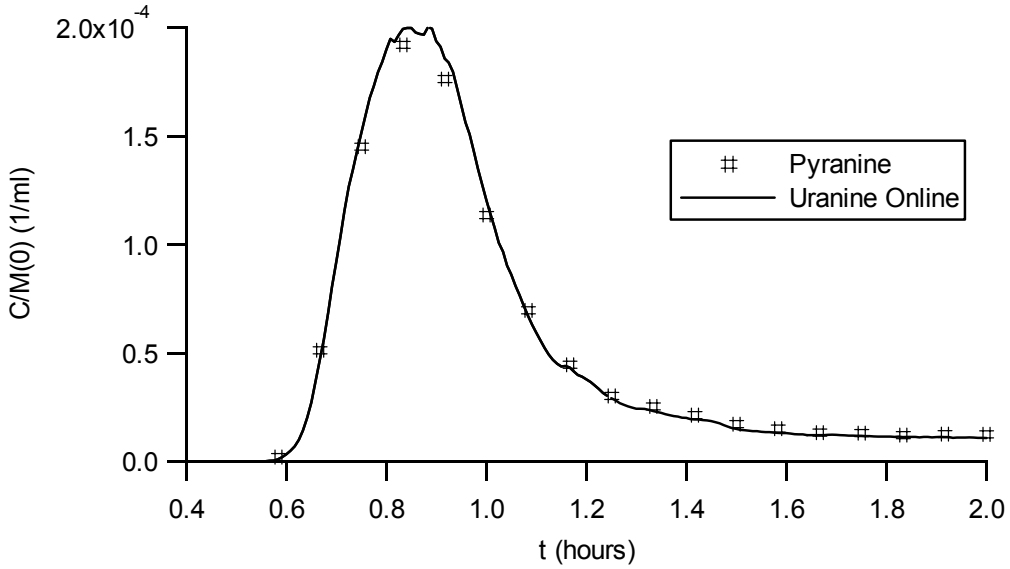
Breakthrough of Uranine and Sulfo Rhodamine G, linear and logarithmic scale

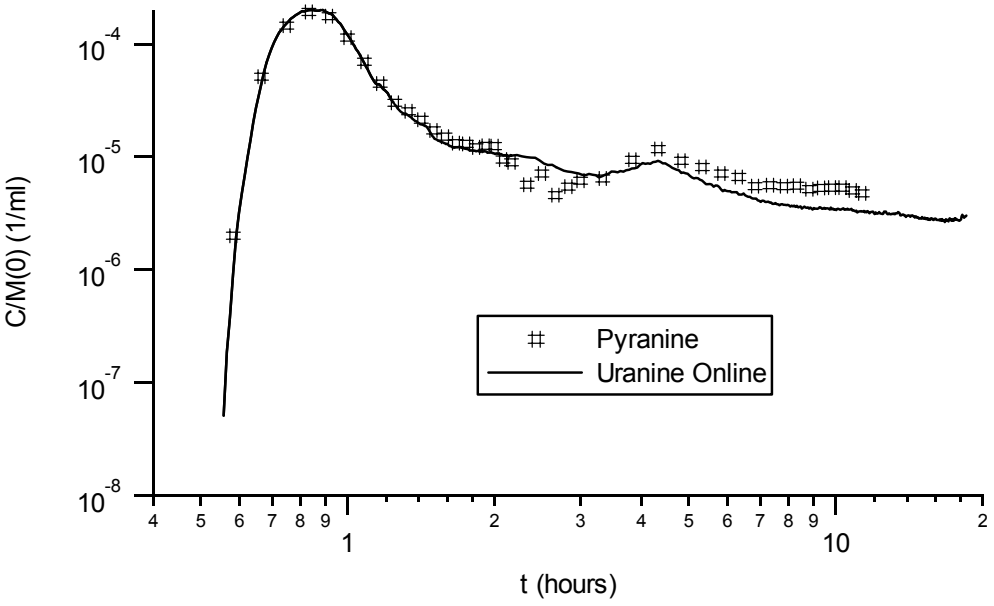




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

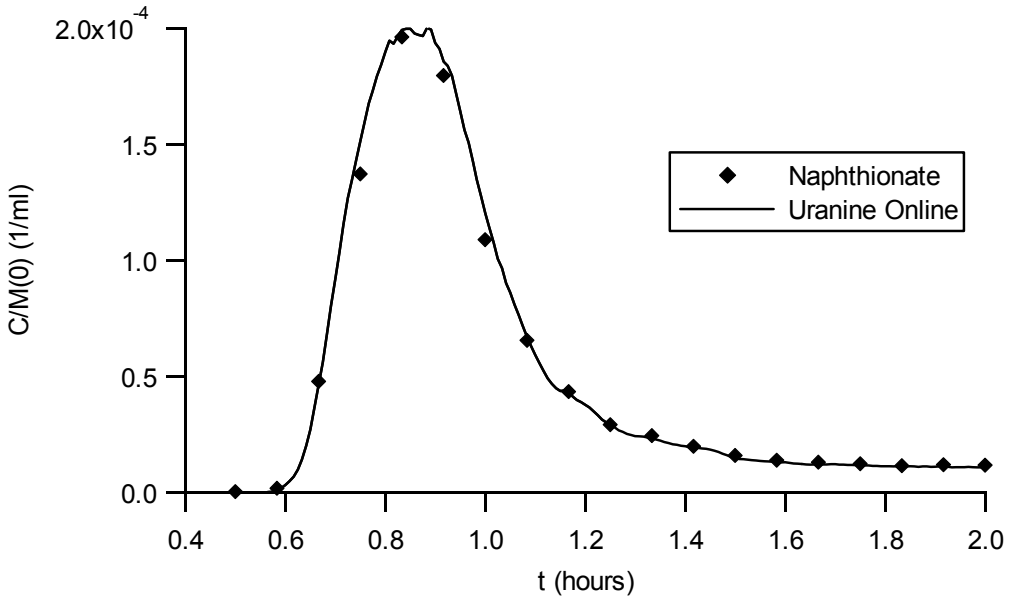
Breakthrough of Uranine and Pyranine, linear and logarithmic scale

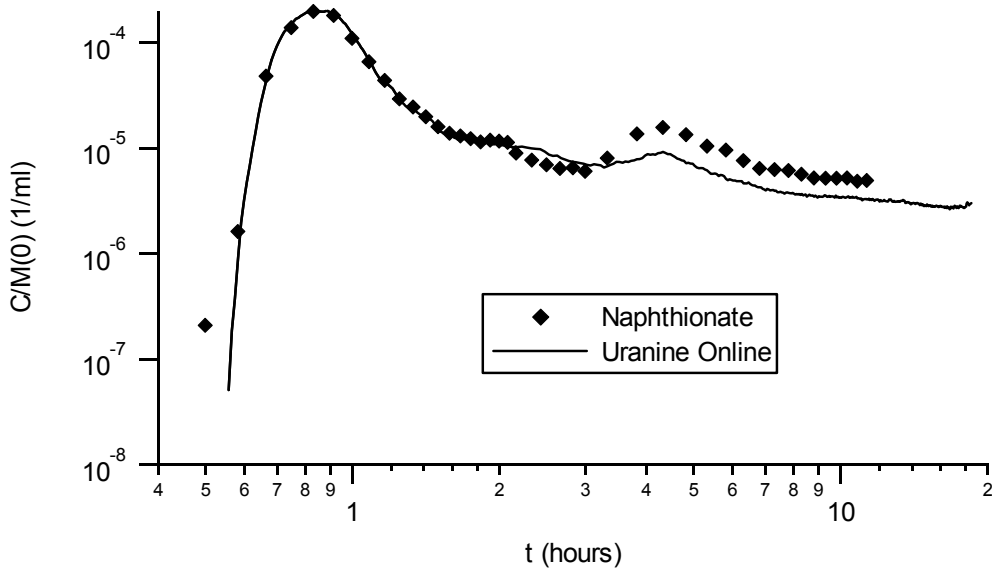




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

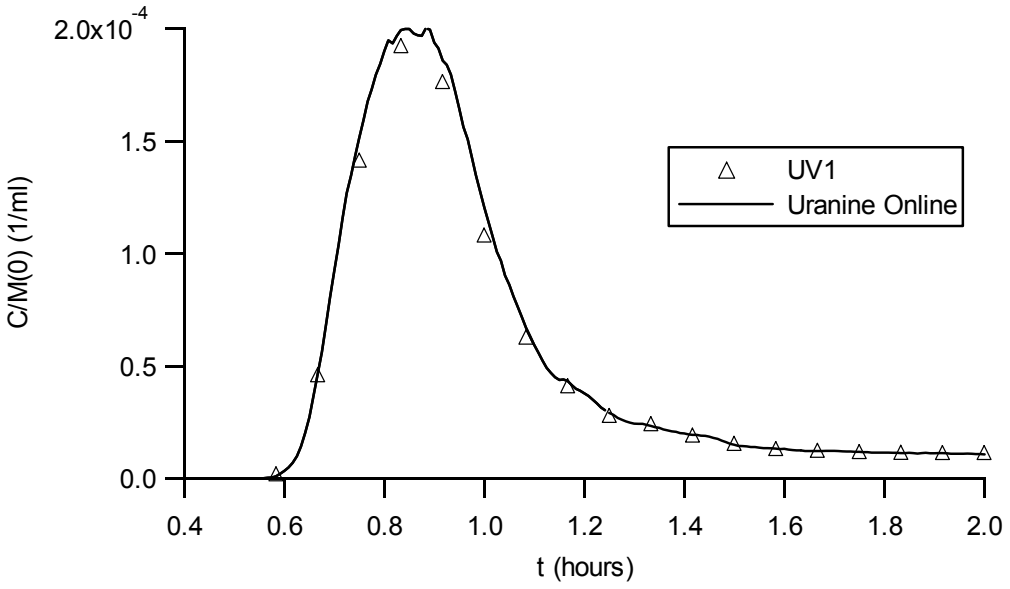
Breakthrough of Uranine and Naphtionate, linear and logarithmic scale

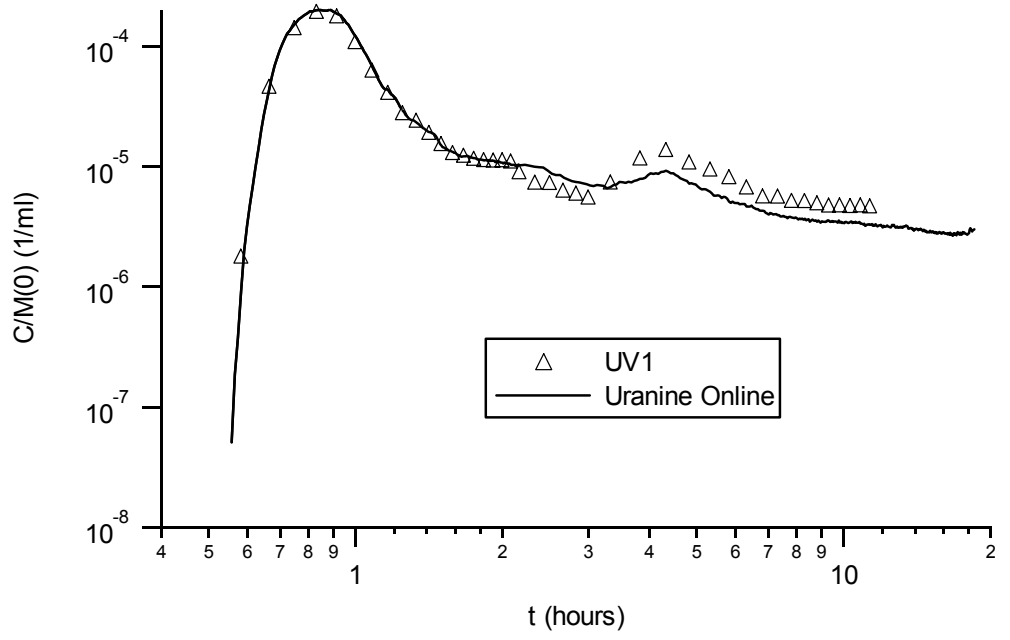




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

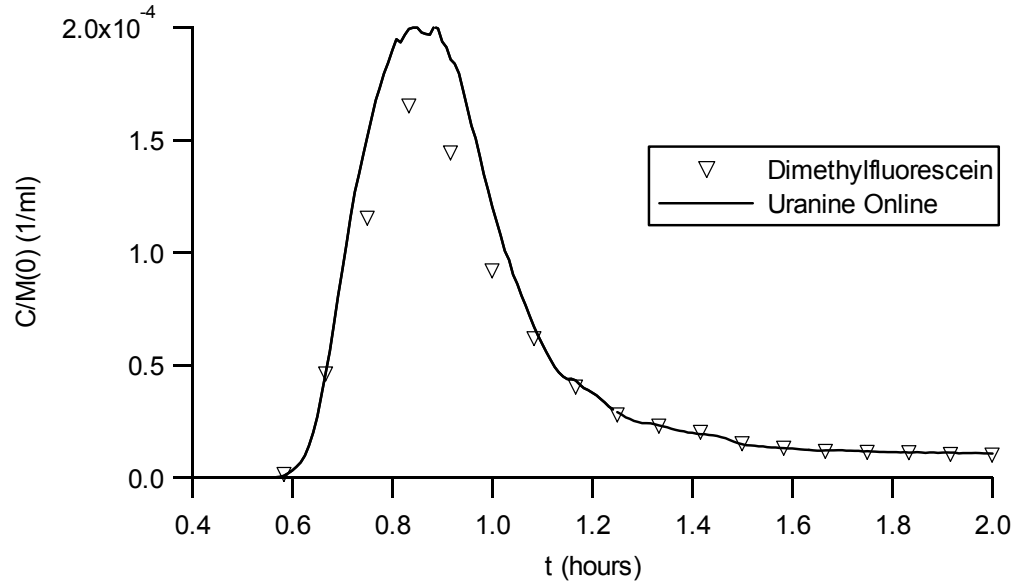
Breakthrough of Uranine and UV1, linear and logarithmic scale

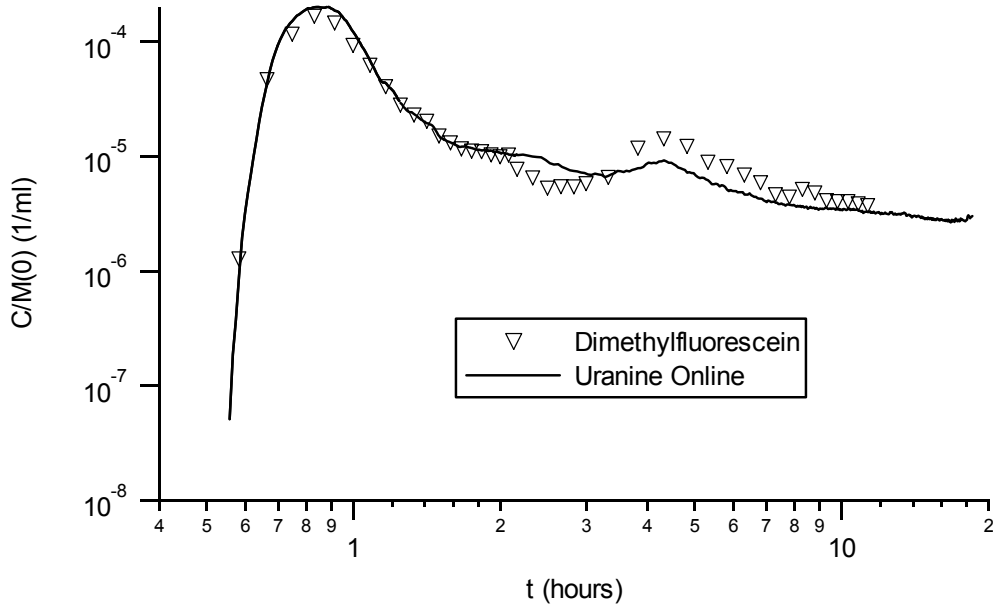




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

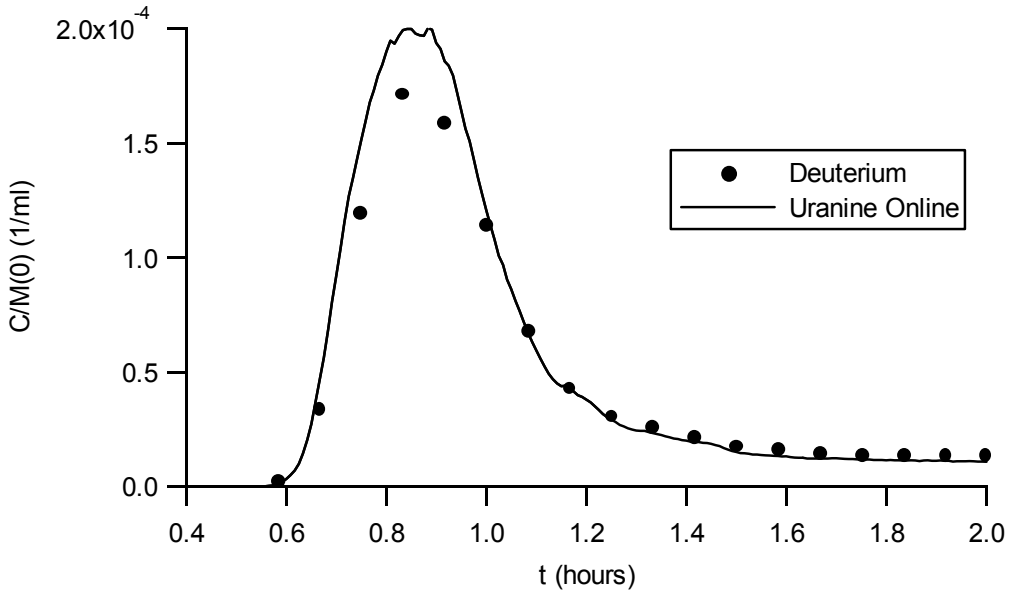
Breakthrough of Uranine and Dimethylfluorescin, linear and logarithmic scale

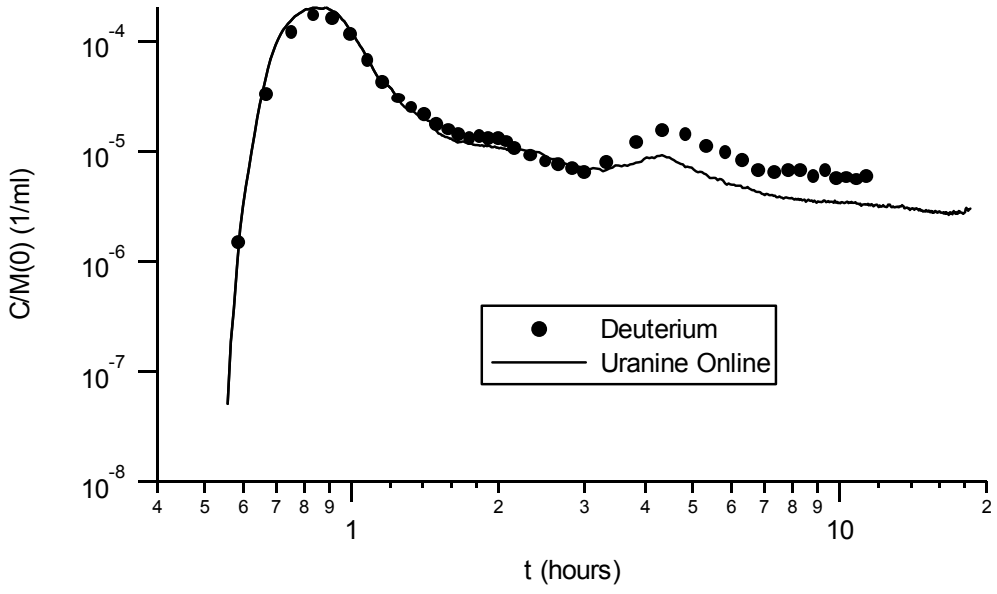




Project: Äspö Tracer Test 1	SOLEXPERTS			
Extraction Side: Borehole KXPP4 Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	09.06.99	tracer_1out

Breakthrough of Uranine and Deuterium, linear and logarithmic scale





Appendix 3

Log Book: Tracer test 2

Log book	**Tracer Test 2**

I. General Setup:	Injection borehole:	KXPP3-Interval R3	
	Extraction borehole:	KXPP4-Interval R4	
	Injection flow rate:	6 ml/min	
	Extraction flow rate:	75 ml/min	
	Tracer used:	He-3, Uranine	
	Tracer input:	Tracer cocktail #1	
	Concentration in tank:	He-3:	1.58 E-04 mbar l/sec
		Uranine	5 ppm (2.05 V)
	Tracer tank volume:	2500 ml	
	Interval volume:	about 5.2 l	
	Data files: tr-test2	Start 4.3.99; 15:01:30	

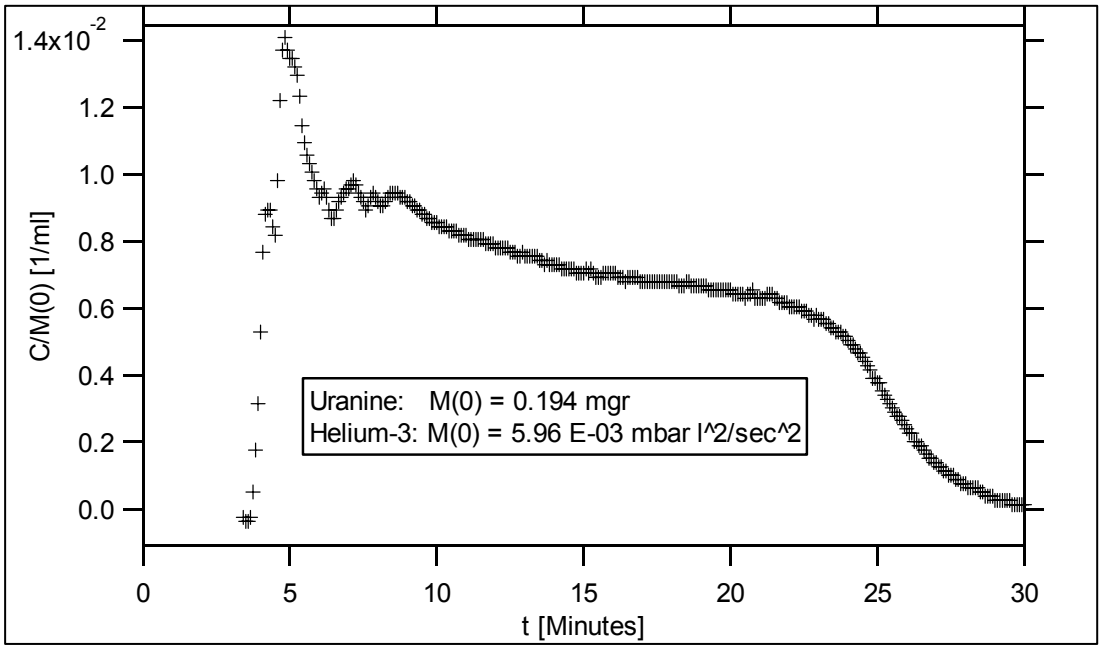
II. Test Schedule:			
date	time	activity	comments
04.03.99	10:30 to 13:00	Flushing exchange line after stopping tracer test 1: Q = 180 ml/min for 2,5 h	
	10:19 to 10:20	Measuring Uranine background at the injection site	
	10:38 to 10:43	Flushing injection line (aprox. 5 l) by decompression (opening the valve)	
	10:40 to 13:00	Calibration of the He-3 and Uranine signal for tracer test 2 (tracer # 1)	
		Injection side: Uranine: 2.05 V = 5 ppm; He-3: 1.58 E-04 mbar l/sec	
		Extraction side: (Tracer 75 times diluted) Uranine 14.5 V = 6.7 ppb He-3: 2.1 E-06 mbar l/sec (Dosage range: 1 ml/min)	
	11:47 to 11:52	Flushing extraction line by decompression	
	12:50	Start dipole injection flow: 6 ml/min	
	15:01:30	Start data file: tr-test2	
	15:02:45	Start tracer injection: Circulation at 250 ml/min	
	15:07:00	First arrival of Uranine at the injection fluorescence flow through cell	
	15:07:30	Tracer injection tank closed and fluid exchange bypass opened	
	15:32	First arrival of Uranine and He-3 tracer at the extraction side	
	15:35	Switch and re-switch the range at the fibre optic fluorometer (only injection side)	
	15:51	Uranine peak at the extraction site	
	15:53	He-3 peak at the extraction site	
	15:58:30	Fluid exchange bypass closed and circulation pump shut off	
05.03.99	09:31	End of data file	
	09:32	Stop flow field and end of tracer test 2	
	10:01	Measuring He-4 by opening the extraction line;	data file: He_4.dat (start: 9:59)
		He-4: 3 E-06 mbar l/seg (about 5 V)	
	10:03	Extraction line completely open (atmospheric pressure): No air bubbles observed	
	10:07	Outflow at 540 ml/min and He-4 at 7.1 to 7.2 E-06 (aprox. 8.5 V)	
	10:12	Stop measuring He-4	

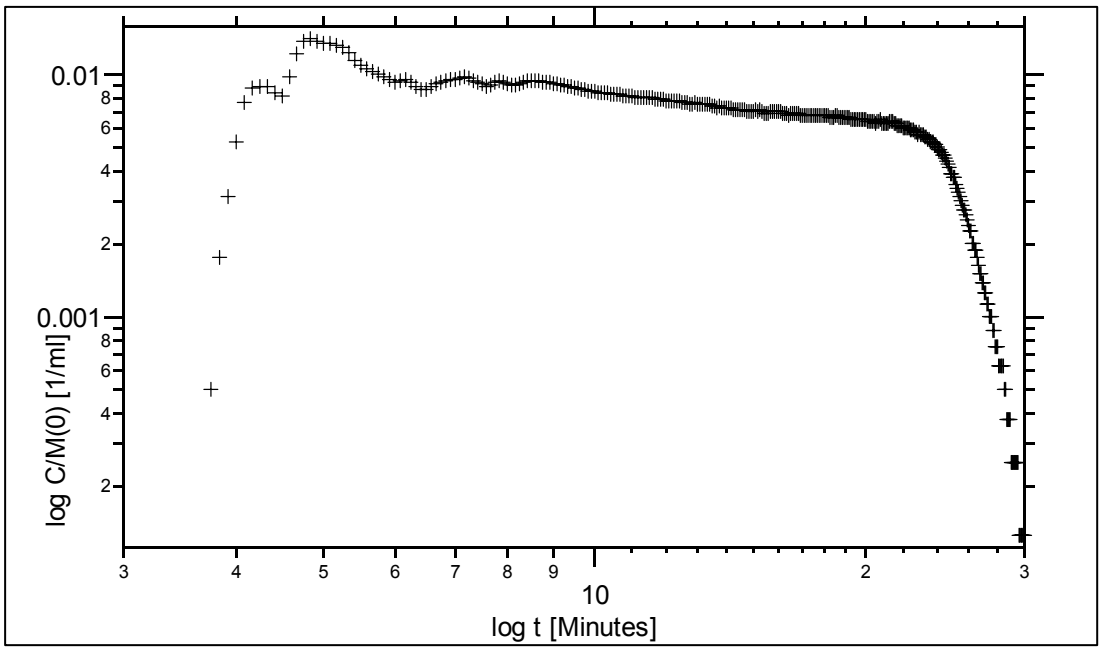
Plots: Tracer test 2

- Tracer input, linear and logarithmic scale
- Breakthrough of Uranine and Helium, linear and logarithmic scale

Project: ASPÖ Tracer Test 2	SOLEXPERTS			
Injection Side: Borehole KXPP3-Interval R3	Visum	Contr.#	Date	Data File
	TT	1179-4	24.03.99	tracer_2

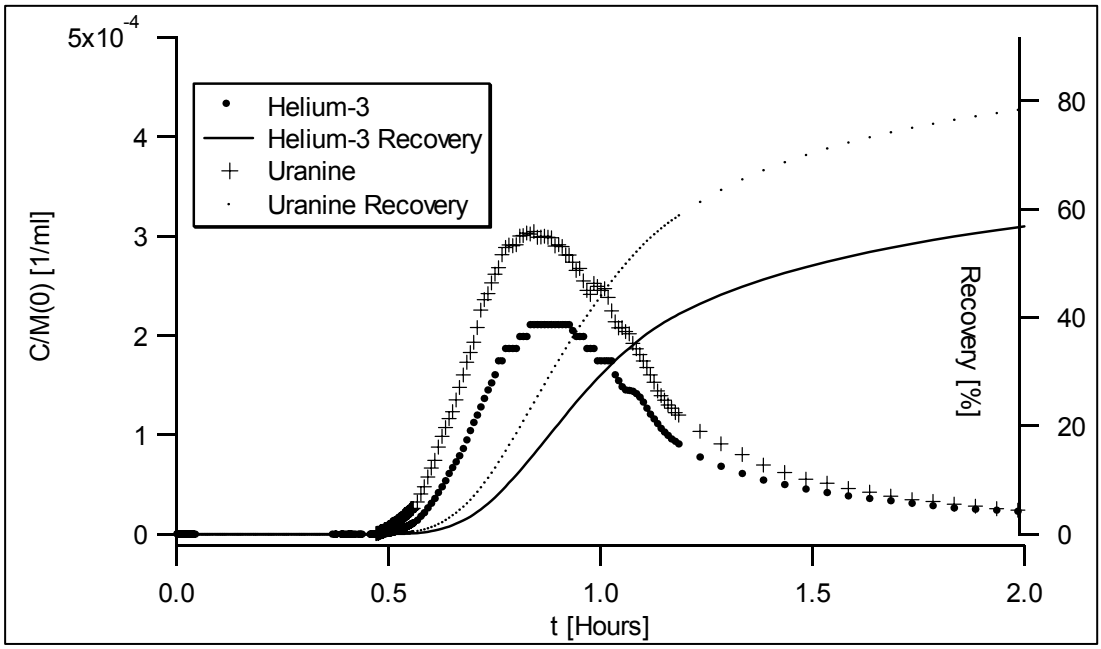
Uranine and Helium-3 Tracer Injection

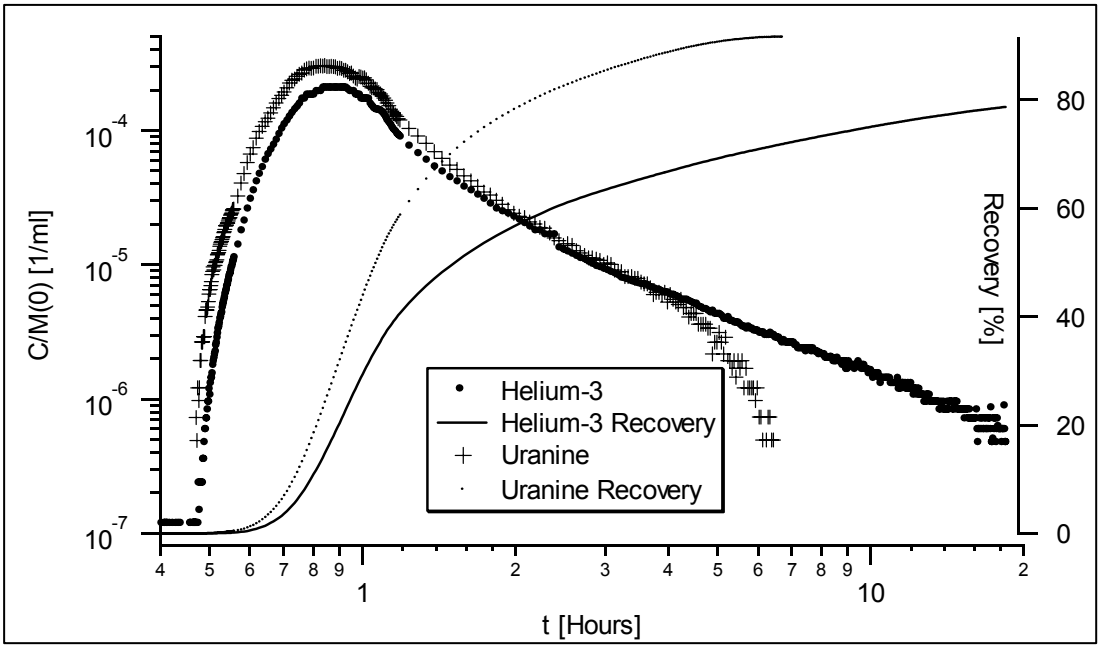




Project: ASPÖ Tracer Test 2	SOLEXPERTS			
Extraction Side: Borehole KXPP4-Interval R4	Visum	Contr.#	Date	Data File
	TT	1179-4	24.03.99	tracer_2

Uranine and Helium-3 Tracer Recovery





Appendix 4

Development of a LC-MS-MS method for measurement of fluorinated benzoic acids

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Introduction

From the measured breakthrough curve of the simultaneously injected Uranine, it could be expected that the breakthrough curve of the fluorinated benzoic acids would give concentrations far below the detection limits estimated by using the HPLC-UV method. It was therefore necessary to apply a column pre-concentration method to obtain a significant decrease of the detection limit, as have been reported by Stetzenbach et al. (1982). In order to increase the selectivity of the detection method, it was proposed change the post column UV-detection to a mass-spectrometer (MS) detector or even to a double mass spectrometric detector (MS-MS). A sub-project was therefore initiated in 2001 in order to develop an improved detection method for the fluorinated benzoic acids acid used in the experiment, i.e., 2,3-Difluorobenzoic acid (2,3-DFBA), 2,6-DFBA, 3,5-DFBA, 2,3,4,5-Tetrafluorobenzoic acid (2,3,4,5-TFBA) and Pentafluorobenzoic acid (PFBA). In the case of obtaining a successful detection method, it was planned this method should be applied on preserved samples from the tracer experiment in 1999.

Experimental

Pre-concentration

Solid phase extraction (SPE) columns (ENV+ 200mg/6ml, IST 915-0020C) were eluted with vacuum on a sample processing station. The columns were conditioned in three steps by pouring three different solutions through the column in the following order:

- 5ml Methanol (HPLC-grade)
- 5ml 50% Methanol
- 15ml distilled water, pH-adjusted to 2.1

The water samples that should be measured (standard solutions and groundwater samples) were adjusted to a pH ~2.1. Each water sample was transferred through a column using a maximum flow rate of 10ml/min. The column was thereafter rinsed with 10 ml distilled water. This step was followed by a second rinsing, using 6ml Methanol, in which the fluorinated benzoic acids were desorbed from the column and were dissolved in the Methanol. The Methanol was collected in a 13ml glass vial and was evaporated to dryness. 0.5ml 0.1M Ammonium acetate (quality: p.a., pH set to 4.5, filtered through a 0.45µm filter) was added to the vial in order to dissolve the residual.

In the pre-concentration step, a volumetric enrichment is thus obtained from the original volume of the sample to 0.5ml. The TRUE Block Scale pilot test samples had a volume of 100 ml, giving volumetric enrichment of a factor 200 just by the pre-concentration step. An additional test was also performed in which additions of the different fluorinated benzoic acids were done to 1 litre samples of Äspö groundwater from the TRUE-1 site. It was found that the enrichment method also worked using 1 litre samples, i.e., a volumetric enrichment of 2000 is possible.

Detection

15µl of the Ammonium acetate sample was injected to a HPLC device (Agilent 1100 with a C-18 column Waters Symmetry 2.1x150mm, acetatebuffer/acetonitrile mixture used as the mobile phase). A triple-quad mass spectrometer (MS-MS detector, Micromass Ultima) was used for the post-column detection of the fluorinated benzoic acids.

In the MS-MS detector, the effluent from the HPLC column is transferred into electro-spay ionic source where the molecules are ionised. The "parent ions" (i.e., the molecular weight minus one) are then separated using the first quadropole mass spectrometer and transferred to a collision cell in which bombardment of the parent ion with argon atom occurs. Daughter ions are produced which afterwards were separated using the second quadropole mass spectrometer system. The most abundant daughter ion mass is selected for the quantification of the different tracers and are thus measured from the effluent of the second mass spectrometer using dynode-detection. The HPLC separation of the molecules in combination with the double selection of masses thus gives a very high selectivity for the different tracers and enables simultaneous measurement of the fluorinated benzoic acids without any interference.

The different mass numbers used for the identification were determined for each fluorinated benzoic acid in a separate experiment and are presented in Table A3-1. The chromatograms for detection process are given in Figure A3-1. The data are obtained from a 1 litre samples with 0.1µg/l of each fluorinated benzoic acid tracer, samples on which the pre-concentration step was applied. As can be seen, the different isomers of DFBA are easily separated by the chromatography. The reason for the variations in the response for the different peaks is explained by the different efficiency for the isomers to form daughter ions of the mass number used in the second mass spectrometry step.

As can be seen when comparing the different chromatograms in Figure A3-1, the elution times of 3,5-DFBA and 2,3,4,5-TFBA are very similar. It is because of the very selective mass spectrometric method applied that selective simultaneous determination of these two tracers can be performed. The efficiency for 2,3,4,5-TFBA to form its selected daughter ion (mass=149) is very high, giving a high signal to noise ratio. For the PFBA, the dimeric form (mass=423) is used for quantification purposes, i.e., is selected in the first mass separation process. Since the number molecules present in the dimeric form is rather low, a rather low number of daughter ions is obtained. However, the low number of interfering atoms abundant in this high mass area causes a very low number of interfering ions at the daughter ion mass (m=167) in the second mass spectrometer. The signal to nose ratio obtained for PFBA is therefore very good and the sensitivity is therefore good.

Table A3-1 Chromatography and mass spectrometry parameters used, together with linearity in the LC-MS-MS detection and the yields obtained in the pre-concentration procedure.

Tracer	Molecular weight	Elution time (min)	Parent ion mass	Daughter ion mass	Linearity, (Correlation coefficient 0.04-40 mg/l)	Yield[1] in the pre-concentration step (%)
2,3-DFBA	158	14.76	157	113	0.99998	66±4
2,6-DFBA	158	5.85	157	113	0.999993	44±3
3,5-DFBA	158	25.76	157	113	0.9998	52±3
2,3,4,5-TFBA	194	25.62	193	149	0.998	75±3
PFBA	212	21.92	423	167	0.99994	44±0

1 Determined at the concentration of 0.1μg/l, standard deviation based on the variation of three samples

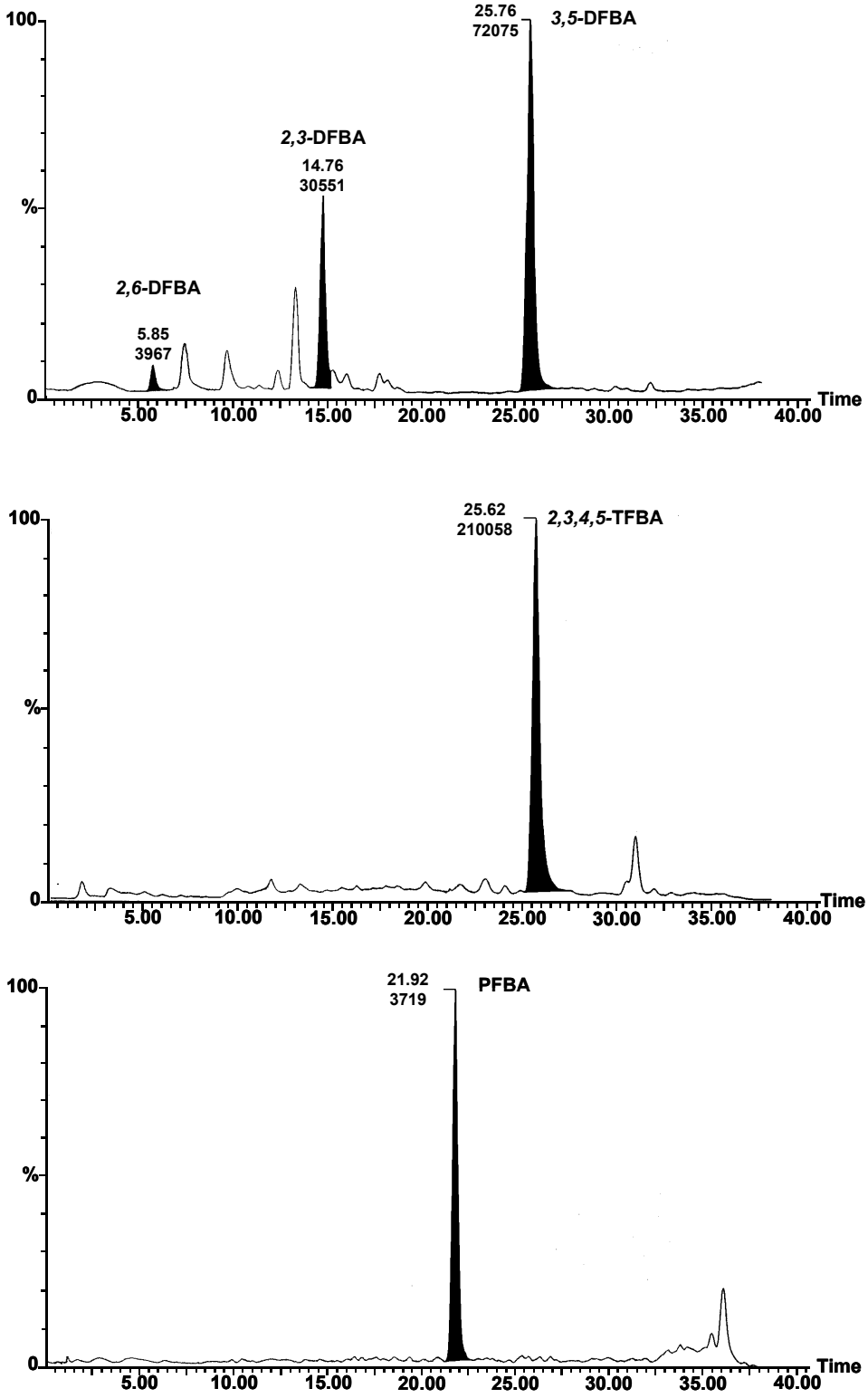

Figure A3-1 *Chromatogram for the LC-MS-MS simultaneous detection of the different isomers of DFBA. A groundwater sample was prepared having a concentration of 0.1μg/l of each fluorinated benzoic acid. The sample was pre-concentrated according to the procedure in the text. The parent/daughter ion masses applied in the detection process were 157/113 (top), 193/149 (middle) and 423/167 (bottom). In the figure, the elution time (in minutes) is given together with the number of daughter ions detected in each quantification peak. The Y-axis gives the response which is automatically adjusted so that the largest peak is set to 100%*

Estimation of a quantification limit

As can be seen in Table A3-1, considerable losses are observed for the pre-concentration step; the yields are significantly lower than 100%. Potential explanations for these losses are irreversible attachment of the fluorinated benzoic acids to the columns and/or losses in the evaporation step. Preliminary tests performed using start concentrations <0.1μg/l indicated that lower amounts of tracer gives lower yield and larger variations. A limited linearity is thus obtained which restricts the possibility to perform quantification in lower concentrations. The repeatability of the pre-concentration step has been checked with three samples of 0.1μg/l of each tracer. The results (Table A3-1) show <4% standard deviation in the yield. From this observation, 0.1μg/l has been estimated as a general quantification limit, i.e., the lowest measurable concentrations.

The linearity in the LC-MS-MS detection has been checked with ammonium acetate samples in the concentration range of 0.04, 0.4, 4 and 40 mg/l, respectively. Considered the yield reported for the pre-concentration step (44-75%) and the volumetric enrichment of a factor 2000, this would correspond to 1 litre groundwater samples with concentrations in the range of 0.03-50 μg/l. The linearity diagrams are shown in Figure A3-2. The correlation coefficients (Table A3-1) are very close to unity, indicating very good linearity in the LC-MS-MS detection process.

The chromatograms obtained for the 0.1μg/l concentrations, Figure A3-1, indicate that detection in concentration at least one order of magnitude should be possible to perform. This means that if a better control of the yield in the pre-concentration step could be obtained, the quantification limit would be significantly decreased. This is especially obvious for the 3,5-DFBA, 2,3,4,5-TFBA and the PFBA, which give very good signal to noise ratio in the chromatograms.

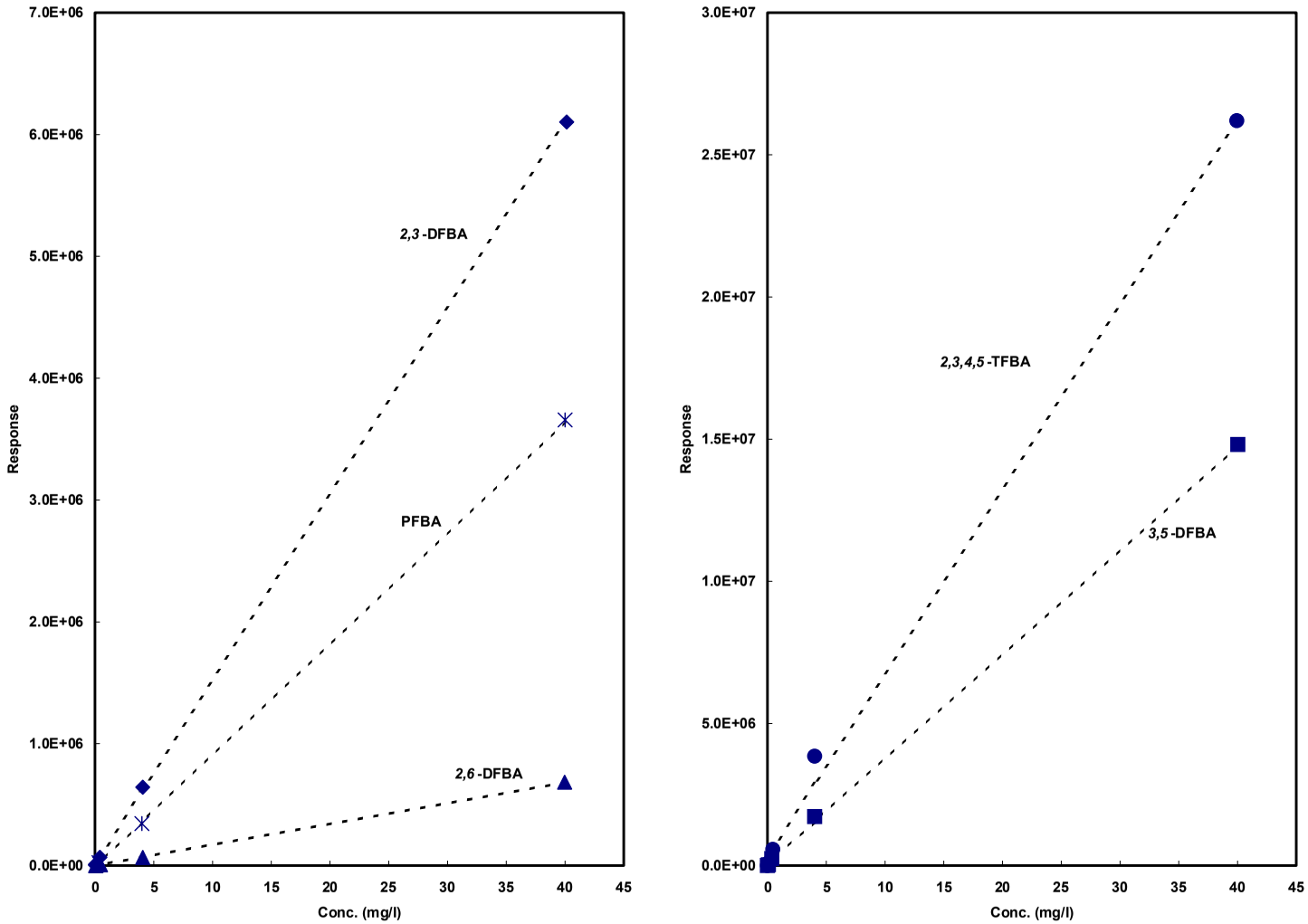

Figure A3-2 *Linearity diagrams for the different tracers for the detection in the LC-MS-MS process.*

Conclusions

The presented method of LC-MS-MS detection has shown to be able to measure the fluorinated benzoic acids reliable >0.1µg/l. Furthermore, it has been shown that by using the method all the five added fluorinated benzoic acids can be measured simultaneously and without any interference from each other. The restrictions in the quantification process are set by the yield of the pre-concentration step. A potential future improvement of the method would be an investigation and optimisation of the parameters in the pre-concentration step, e.g., a more careful reconditioning of the columns used in that procedure.

References

Stetzenbach, K.J., Jensen, S.L., Thompson, G.M. 1982: Trace enrichment of fluorinated organic acids as ground-water tracers by liquid chromatography, Env. Sci Technol. 16, 250-254