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Äspö Hard Rock Laboratory

Project Concrete and Clay

Degradation of organic materials in cementitious environments

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Summary

This report presents the results from 3 different studies on degradation of organic materials in cementitious environments.

The first study presents an investigation of colloid formation through degradation of organic materials which had been stored in cement buffered ground water for a period of about 4 years. In accordance with current theory, the study showed that the number of colloid particles per unit volume of water was similar to the levels found in ordinary tap water.

The second study presents an NMR study of the degradation of different types of organic materials which had been stored in cement buffered ground water for a period of about 6 years. The study showed that degradation had been minute and a high enough concentration degradation products for structure determination to be possible was only found in sample containers containing rubber gloves. The compunds found in these containers could be identified as originating from well-known softeners/plasticisers used in the plastic industry.

The third study presents an investigation of the degradation of organic materials which had been embedded in solid concrete and stored in the bedrock at the Äspö Hard Rock Laboratory for a period of about 8 years. In accordance with the previous study, compunds corresponding to degradation products from softeners used in the rubber industry could be found in concrete which had contained pieces of rubber gloves but in the other specimens no degradation products could be identified. Here, it was also noticed that the identified molecules had diffused in the solid concrete to a distance of between 10 and 20 mm from the rubber gloves.

In all, the studies presented in this report show that degradation of organic materials in cementitious environments is limited during the time period covered by these studies. However, for the rubber gloves, release of the softeners or their degradation products can be expected within a rather short period of time after that the repository has been closed and resaturated. Studies of the effect of this on e.g. radionuclide transport have not been a part of this study but could be considered for further investigations.

Sammanfattning

I denna rapport presenteras resultaten från 3 olika studier rörande nedbrytning av olika typer av organiska material i cementmiljö.

Den första studien presenterar en undersökning av kolloidbildning orsakad av nedbrytning av organiska material vilka förvarats i stålbehållare innehållande cementbuffrat grundvatten under en period av cirka 4 år. I överensstämmelse med aktuell teori visade studien att antalet kolloidala partiklar per volymenhet vatten motsvarade de som återfinns i vanligt kranvatten.

Den andra delen omfattar en NMR-studie av nedbrytning av olika typer av organiska material vilka förvarats i stålbehållare innehållande cementbuffrat grundvatten under en period av cirka 6 år. Studien visade att nedbrytningen varit mycket liten och endast i provbehållare innehållande bitar av gummihandskar kunde nedbrytningsprodukter hittas i en tillräckligt hög koncentration för att identifiering av de kemiska föreningarna skulle kunna vara möjlig. Studien visade här att de identifierade ämnena kunde hänföras till kända mjukgörare använda inom tillverkningsindustrin vilka frigjorts under experimentperioden.

Den tredje delen av denna rapport omfattar en studie av nedbrytningen av organiska material vilka varit inneslutna i solid betong mättad med salint grundvatten och som har lagrats i berggrunden vid Äspölaboratoriet under en period av cirka 8 år. I överensstämmelse med resultaten från den tidigare studien kunde nedbrytningsprodukter från de organiska materialen endast hittas i betong som hade innehållit bitar av gummihandskar och vilka har sitt ursprung i samma typ av mjukgörare som återfanns i stålbehållarna. Här noterades även att diffusion av dessa molekyler i den fasta betongen till ett avstånd mellan 10 och 20 mm från gummihandskarna ägt rum. I övriga behållare kunde inga nedbrytningsprodukter som kunde härledas till det organiska materialet detekteras.

Sammantaget visar studierna i denna rapport att nedbrytning av organiska material i cementmiljö är mycket begränsad under de tidsperioder som omfattats av detta arbete. För gummihandskar kan dock frisättning av mjukgörare eller nedbrytningsprodukter därav förväntas inom en ganska kort tidsperiod efter det att förvaret har återmättats. Studier av effekten av detta på t ex radionuklidtransport har inte varit en del av denna studie men kan övervägas för framtida undersökningar.

Contents

1 Introduction

1.1 Background

Low and intermediate level radioactive waste, LILW consists of a complex mixture of different types of materials including both organic as well as inorganic materials. Prior to disposal, the waste is placed in different types of containers which are also filled with a conditioning material, e.g. cement or bitumen. In Sweden, LILW is deposited in the final repository for short-lived radioactive waste, SFR, or stored temporarily while waiting for the final repository for long-lived radioactive waste, SFL, to be completed and taken into operation.

In SFR which has been in operation for about 30 years, concrete and other cement based materials are extensively used in the engineered barrier system, either alone or in combination with bentonite as in the Silo (SKB 2015). In SFR a majority of the waste is conditioned in a cement matrix but some is instead conditioned in bitumen. A certain fraction of the ion exchange resins deposited in the waste vaults for concrete tanks, 1BTF and 2BTF is just dewatered and placed in concrete tanks without any additional conditioning material.

For SFL which is currently planned to be taken into operation around the year 2045 the SFL concept study finalised in 2013 (Elfwing et al. 2013) suggested that the core components as well as the PWR reactor pressure vessels from the nuclear power plants should be disposed of in a waste vault in which the engineered barrier system is based on the use of concrete alone. The legacy waste currently stored at the Studsvik site and which comprises a complex mixture of different materials and nuclides was suggested to be disposed of inside a concrete structure which is surrounded by a thick layer of bentonite on all sides as the main barrier material in this waste vault.

Once the repositories have been filled with waste, the rock vaults and transport tunnels will be backfilled with different types of materials, e.g. crushed rock or bentonite. Also large plugs will be constructed to limit water transport in the tunnels and rock vaults. Once the drainage pumps have been turned off, water will slowly fill the repository, saturating the voids and pore systems of the porous materials.

During the long periods of time covered by the safety analyses interactions between the groundwater and species dissolved in the groundwater and the materials in the repositories will occur. These interactions will cause changes in the physical and chemical properties of the barrier materials as well as degradation of the waste leading to the formation of species that may further affect the properties of the materials in the engineered barriers. Besides affecting the properties of the materials in the engineered barriers, low molecular organic degradation products may also affect the retaining capacity of the barrier systems through complexation with the radionuclides.

In the case of waste containers containing ion exchange resins conditioned in bitumen, the chemical conditions will be very different in the containers compared to the cement equilibrated groundwater. Here, concerns have been made that colloids (particles with dimensions in the 1–1 000 nm range) to which radioactive elements may sorb will be released from the bitumen, thus enhancing radionuclide transport rates.

However, the chemistry of cement equilibrated water (i.e. water that has equilibrated with cement in the barriers) is characterised by high ionic strength and a pH from 10 to 12 corresponding to $[OH^-]$ of 10^{-4}–10^{-2} M. Under these conditions, colloid formation is normally inhibited (Israelachvili 2011) but as the ionic strength limit for colloid formation and colloid stability is material specific investigations for each material combination is required for certainty.

1.2 Project objectives

The objective of the experiments presented in this report – all being parts of the project "Concrete and Clay" – is to increase the understanding of the processes that occur when organic materials present in the waste interacts with the cementitious materials used in the conditioning grout and the engineered barriers under the influence of an anoxic groundwater.

1.3 Concrete and clay – experimental concept

During the time period 2010–2014 a total of 9 experiment packages comprising concrete cylinders or bentonite blocks each containing different material specimens representative of low and intermediate level radioactive waste were installed in 3 different tunnels in the Äspö Hard Rock Laboratory according to the following:

- **Concrete and clay phase 1 comprising field scale concrete experiments** – 2 experiment packages, each containing 3 concrete cylinders with material specimens (both organic materials and metals).
- **Concrete and clay phase 2 comprising field scale concrete experiments** – 1 experiment package containing 3 concrete cylinders with material specimens (both organic and metals) and one package containing concrete cylinders without material.
- **Concrete and clay phase 3 comprising field scale bentonite experiments** – 5 experiment packages, each containing 30 bentonite blocks each of which also containing 4 small cylinders made of standard or low-pH cement paste or a solid cylindrical specimen made of carbon steel or stainless steel. The vast majority of the small cylinders also contain a metal powder (Fe, Ni, Cr, Mo) or a powder of a metal chloride ($CsCl$, $SrCl_2$, $EuCl_3$) but a few are used as blanks without any additional material.

The experiments are illustrated in Figures 1-1 and 1-2 and fully described in Mårtensson (2015).

As a complement to the field scale concrete experiments also smaller laboratory scale experiments are carried out. The laboratory scale experiments comprise a total of 20 stainless steel containers which all are filled with about 1 000 ml of Äspö groundwater, about 50 grams of crushed hardened cement paste and material specimens of the same type as used in the field scale concrete experiments.

The purpose of the laboratory scale experiments is to provide an indication on the extent of degradation of the waste over time. By analysing the water in the containers a suitable time for the retrieval of the field scale concrete experiments can be obtained.

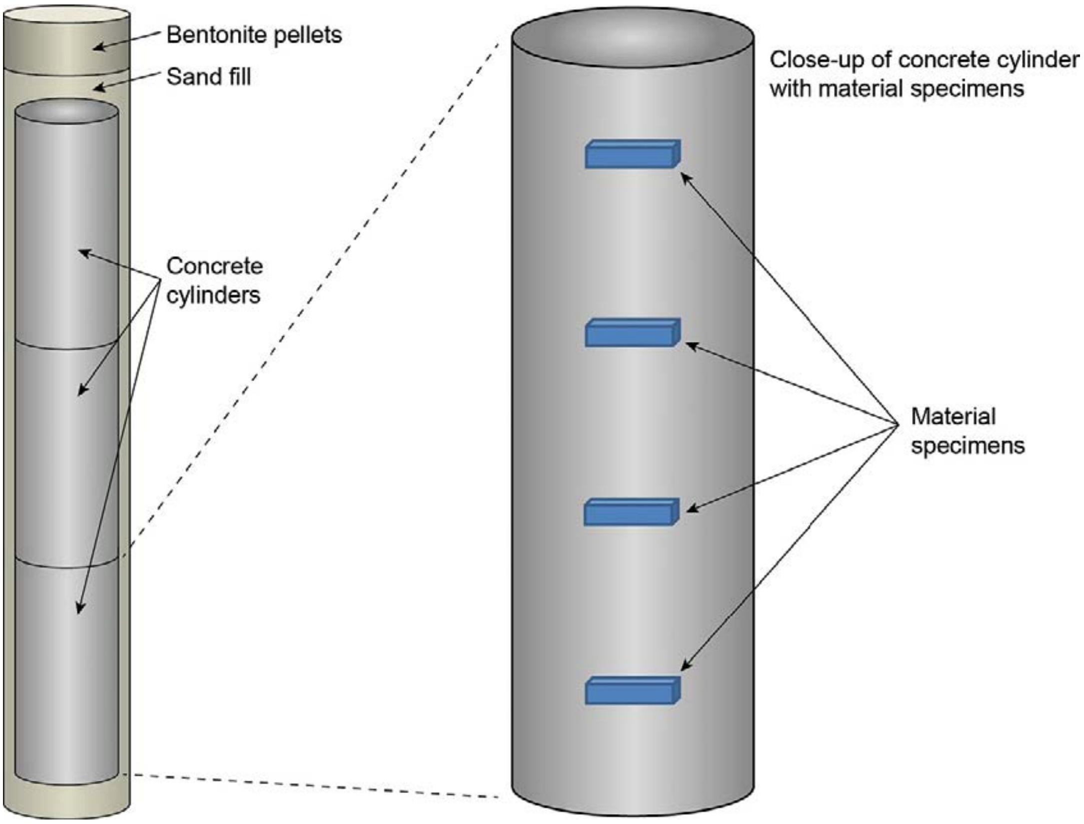

Figure 1-1. *A schematic illustration of the field scale concrete experiments.*

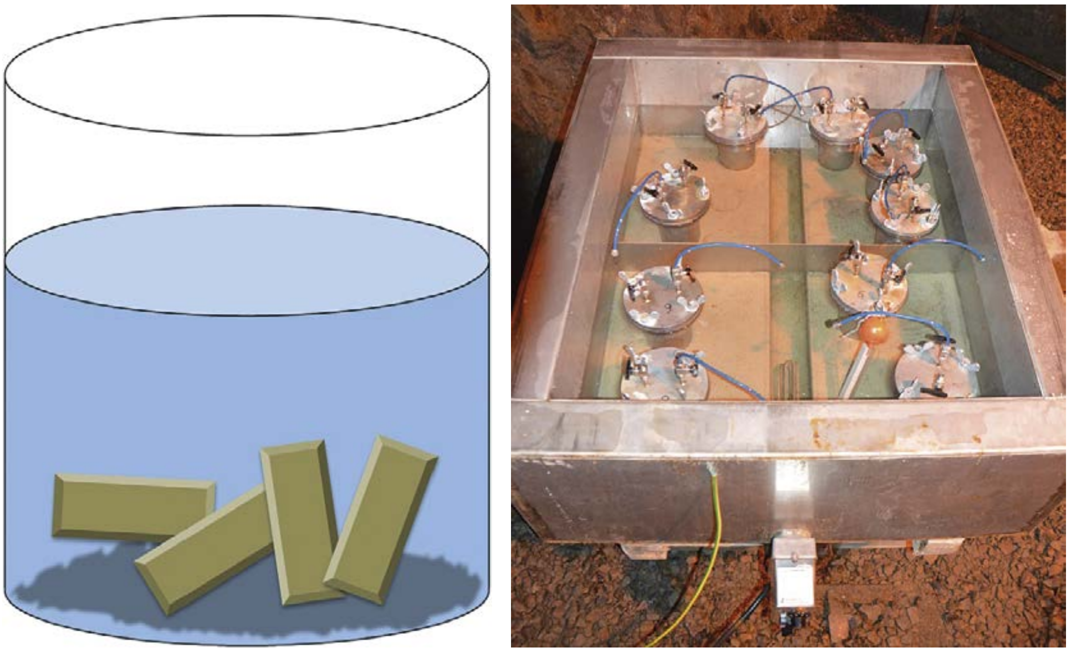

Figure 1-2. *A schematic illustration of the laboratory scale experiments (left image) and the heater used to keep the temperature in some of the experiments at about 50 °C. During operation the heater is also provided with an insulating lid.*

1.4 Description of the experiments in this study

1.4.1 Laboratory scale experiments

Of the 20 steel containers that were prepared by Mårtensson (2015) the containers presented in Table 1-1 were selected for analyses in the work presented in this report.

Table 1-1. Content of the steel containers analysed in this report.

Steel container	Material type	Dimensions	Weight (g)	Temperature (°C)
1	Cotton, cloth from overall	Total area: 381.6 cm^2 Thickness 0.40 mm	7.1	50
2	Paper	Total area 500 cm^2 Thickness 0.07 mm	0.66	50
3	Rubber (gloves)	Total area 432 cm^2 Thickness 0.40 mm	15.9	50
4	Plastic bag	Total area 372.5 cm^2 Thickness 0.04 mm	1.5	50
5	Ion exchange resin (Carboxylate)	Powder	25.0	50
6	Ion Exchange Resin (Anion)	Powder	25.0	50
7	Ion Exchange Resin (Sulphonate)	Powder	25.0	50
8	Filter Aid (UP2)	Powder	15.0	50
9	Bitumen	Total volume 10.0 ml Diameter of individual drops 3–8 mm	10.0	50
10	Ion exchange resin (Carboxylate)	Powder	25.0	22/12*
17	Rubber (gloves)	Total area 432 cm^2 Thickness 0.40 mm	15.9	22/12*
19	Reference 1	Contains only 50 g of Ordinary Portland Cement, OPC, and Äspö ground water		

* The temperature in the cement laboratory at Ringhals NPP where the containers were initially stored and in the Äspö tunnel was about 22 °C and 12°C respectively.

1.4.2 Field scale concrete experiments

The work covered in this study comprise analyses of 2 concrete cylinders denoted I-2B and I-3B which were emplaced in installation hole KR0009G01 in TASR for a total of about 8 years. Each concrete cylinder contain specimens of 4 different types of materials according to Tables 1-2 and 1-3.

The specimens in concrete cylinder I-3B were simply placed directly in the wet concrete. However, the specimens placed in concrete cylinder I-2B required a little more preparatory work. Both the ion exchange resins and the filter aid were mixed with cement mortar and cast into solid samples in small plastic cups as shown in Figure 1-3. In this process, ethylene glycol was used as an additive as will be discussed later in this report. For further details concerning the specimen preparation; see Mårtensson (2015).

Figure 1-3. *Cement specimens containing UP2 filter aid.*

Table 1-2. Specimens in concrete cylinder I-2B.

Distance from bottom of cylinder (cm)	Type of material	Specimen name*
85	Ion Exchange Resin, Sulphonate	SA3
85	Ion Exchange Resin, Sulphonate	SA4
60	Filter aid, UP2	UP2a3
60	Filter aid, UP2	UP2a4
35	Ion Exchange Resin, Anion	SB3
35	Ion Exchange Resin, Anion	SB4
10	Ion Exchange Resin, Carboxylate	WA3
10	Ion Exchange Resin, Carboxylate	WA4

* Specimen name refers to Table A-3 in Mårtensson (2015).

Table 1-3. Specimens in concrete cylinder I-3B.

Distance from bottom of cylinder (cm)	Type of material	Amount
85	Plastic bag (blue and transparent)	5 pieces, each 50 × 100 mm
60	Rubber gloves (blue)	5 pieces, each 50 × 50 to 100 × 100 mm
35	Cotton fabric from overalls (blue and yellow)	5 pieces, each about 25–90 cm^2
10	Paper (for wiping)	5 pieces, each a few grams

1.5 Purpose and scope of the work presented in this report

The purpose of the work presented in this report is to investigate the extent to which different types of organic materials have degraded in a cementitious environment and the extent of diffusion of the degradation products in solid concrete.

The work presented in this report covers the following aspects:

- Degradation of different types of organic materials in cement buffered ground water.
- Degradation of different types of organic materials in solid concrete saturated with saline ground water.
- Diffusion of degradation products in solid concrete.

Based on the information obtained from this work plans will be made for retrieval and analyses of the remaining experiments involving solid concrete cylinders containing organic materials.

1.5.1 Investigation of colloid release from organic materials in cement buffered ground water

It is well known that cement-equilibrated water provides water chemistry with high ionic strength and a pH from about 10 to 12 corresponding to $[OH^-]$ of 10^{-4}–10^{-2} M depending on the solid: water ratio. For solid concrete pH in the pore water is expected to be about 12.5 as controlled by the dissolution of portlandite, $Ca(OH)_2$. A high pH (high $[OH^-]$) also gives the solution a high ionic strength. Higher ionic strength promotes aggregation and sedimentation of colloids; hence the concentration of colloids in high ionic strength solution is expected to be low. However, the ionic strength limit for colloids to be stable in solution is specific and has to be determined experimentally for each type of particles.

In theory the ionic strength limit for colloids to be able to stay out in solution can be calculated with DLVO theory (Israelachvili 2011). In complex natural systems the calculations are difficult to solve since the uncertainties are large in the parameters to be included. Therefore experimental studies under the actual chemical and physical conditions are required.

The purpose of this study is to investigate colloid release from ion exchange resins and filter aid in cement buffered ground water and to evaluate the risk for extensive colloid formation in this system.

1.5.2 NMR studies of degradation of organic materials in cement buffered ground water

Through degradation of organic materials in cementitious environments organic molecules which may affect the retention capability of the engineered barriers may be released. An example is the formation of isosaccharinic acid which is formed through chemical degradation of cellulose but also other chemical compounds can be formed through the degradation of other types of organic materials.

The purpose of this study is to investigate the degradation of different types of organic materials stored in cement buffered ground water through an NMR investigation of organic degradation products in the water phase. The results from this study will be used in the planning of retrieval and analysis of the solid concrete cylinders discussed in the following section.

1.5.3 Studies of degradation of organic materials in solid concrete

The work introduced in Section 1.5.2 concerned studies of degradation of organic materials under conditions characterised by a large excess of water but with limited amounts of cementitious materials. However, the conditions in a repository just after closure are characterised by a low availability of water but with, in principle, unlimited access to cement minerals.

The purpose of studying the degradation of organic materials embedded in solid concrete is to gain a deeper understanding of how the waste degrades under repository like conditions but also to study the diffusion of the degradation products in the concrete.

1.6 Structure of this report

This report is divided into 5 chapters and 3 appendices with the following content:

Chapter 1 – Chapter 1 presents a general background to the project Concrete and Clay and a description of the experiments analysed in the work presented in this report. This chapter also presents the purpose and scope of this report.

Chapter 2 – Chapter 2 presents details on retrieval of the experiments and preparation of the specimens before being sent to the laboratories for further preparation prior to analysis.

Chapter 3 – Chapter 3 presents the experimental details including methods for sample preparation and analyses.

Chapter 4 – Chapter 4 presents the results from the different studies.

Chapter 5 – Chapter 5 finally presents a summary of the results and conclusions.

Appendix A – Appendix A presents an investigation of colloid release from cement grout in which colloidal silica had been used as a stabilising agent. This work is not a part of the project "Concrete and clay" but as this analysis was performed as a part of the work presented in this report the results are reported here for completeness.

Appendix B – Appendix B presents complementary details from the analyses presented in Section 4.2.

Appendix C – Appendix C presents complementary details from the analyses presented in Section 4.3.

2 Retrieval and specimen preparation

2.1 Laboratory scale experiments

Retrieval of the laboratory scale experiments comprised selecting the containers of interest and placing them in a box which was sent to the laboratory, Figure 2-1. All further sample preparation techniques used prior to analysis are described in the relevant sections.

Figure 2-1. *Steel containers placed in the transport box.*

2.2 Field scale concrete experiments

2.2.1 Retrieval and packaging

As a first step, the bolts holding the beams securing the lid were unscrewed and the concrete lid removed, Figure 2-2. Thereafter, the top sand was removed by means of a powerful vacuum cleaner and the top concrete slab which separates sand and the bentonite that seals the gap between the concrete foundation and the bedrock was removed. Finally, the bentonite was dug out. At this point free standing water was observed in the hole, Figure 2-2.

The most exhausting part of the retrieval turned out to be removal of the sand from the slit between the concrete cylinders and the wall of the installation hole. Attempts to lift the concrete cylinders without prior removal of the sand were unsuccessful and the cylinders remained stuck in the installation hole. Different methods were used to loosen up the sand, but none was really successful on its own. This – in combination with the gap being both narrow and deep – made the work both exhausting and relatively time consuming. However, eventually enough sand had been removed for retrieving the concrete cylinders, Figures 2-3 to 2-5.

After the lift, the concrete cylinders were wrapped in plastic, placed on a pallet and transported up to the laboratory for sectioning, packaging and labelling, Figure 2-5.

Figure 2-2. *The concrete lid is removed (left image). After removing the top seal, free standing water was found in the installation hole, indicating that saturation of the concrete cylinders has been sufficient.*

Figure 2-3. *Cleansing of the sand filled slit between the concrete cylinders and the wall of the installation hole.*

Figure 2-4. *Lift of a concrete cylinder.*

Figure 2-5. *The concrete cylinders have been placed on a pallet for transport.*

2.2.2 Sectioning and core drilling

In the experimental hall in the above ground facilities at Äspö, the concrete cylinders were each sectioned into four parts, Figure 2-6, each containing samples of one particular type of organic material, Tables 1-2 and 1-3. The different parts were numbered from 1 (top) to 4 (bottom).

After sectioning, core drilling was carried out through the individual parts. Drilling was carried out "at random" in the longitudinal axis of the cylinder using a ∅ 50 mm core drill. The reason for this was that the cylinders lacked a reference point and it was therefore not possible to use the images from the casting to find the material specimens. A number of cores were drilled in each section until a core with a sufficient amount of specimen material was found. The cores were then labelled before further sample preparation, Figure 2-7.

Figure 2-6. *The concrete cylinders after sectioning.*

Figure 2-7. *Drill cores from the different parts of the concrete cylinders containing different types of material specimens.*

2.2.3 Sample preparation

The sample preparation comprised cutting and crushing. Cutting was carried out with a water-cooled saw in the preparation lab at the Äspö laboratory according to Figure 2-8. For some cores the positions of the cuts were slightly adjusted. This was due to that the material specimens were not always in the middle of the longitudinal direction of the core. The samples were numbered according to Table 2-1, Figure 2-9. At this point all material specimens except for those containing ion exchange resins and filter aid were removed. The final step in the sample preparation consisted of crushing the samples in a jaw crusher down to a grain size of about 0.1 mm and placing the crushed material in plastic containers, Figure 2-10.

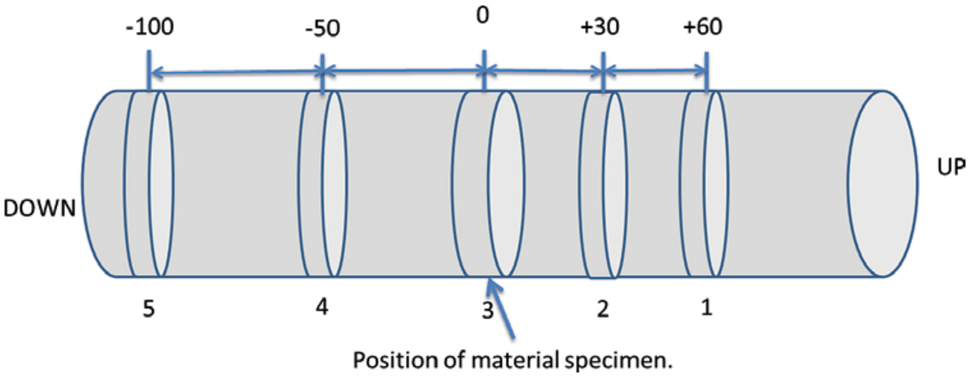

Figure 2-8. *Illustration showing how the cores were sectioned. The diameter of the core is 50 mm.*

Figure 2-9. *Specimens containing samples with filter aid mixed with cement (left) and a piece of a cotton fabric from an overall (right).*

Figure 2-10. *Specimen ready to be sent for analysis.*

Table 2-1. Specimen ID after sectioning and crushing.

Specimen ID	Concrete Cylinder	Material specimen	Specimen name*	Distance from material specimen (mm)
FXM000805	I-2B	Ion exchange resin, sulfonate	SA3 and SA4	60
FXM000806	I-2B	Ion exchange resin, sulfonate	SA3 and SA4	30
FXM000807	I-2B	Ion exchange resin, sulfonate	SA3 and SA4	0
FXM000808	I-2B	Ion exchange resin, sulfonate	SA3 and SA4	50
FXM000809	I-2B	Ion exchange resin, sulfonate	SA3 and SA4	100
FXM000810	I-2B	Filter aid UP2	UP2a3 and UP2a4	60
FXM000811	I-2B	Filter aid UP2	UP2a3 and UP2a4	30
FXM000812	I-2B	Filter aid UP2	UP2a3 and UP2a4	0
FXM000813	I-2B	Filter aid UP2	UP2a3 and UP2a4	50
FXM000814	I-2B	Filter aid UP2	UP2a3 and UP2a4	100
FXM000815	I-2B	Ion exchange resin, anion	SB2 and SB3	60
FXM000816	I-2B	Ion exchange resin, anion	SB2 and SB3	30
FXM000817	I-2B	Ion exchange resin, anion	SB2 and SB3	0
FXM000818	I-2B	Ion exchange resin, anion	SB2 and SB3	50
FXM000819	I-2B	Ion exchange resin, anion	SB2 and SB3	100
FXM000820	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	60
FXM000821	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	30
FXM000822	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	0
FXM000823	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	50
FXM000824	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	100
FXM000825	I-3B	Plastic bags		10
FXM000826	I-3B	Plastic bags		30
FXM000827	I-3B	Plastic bags		0
FXM000828	I-3B	Plastic bags		50
FXM000829	I-3B	Plastic bags		100
FXM000830	I-3B	Rubber gloves		10
FXM000831	I-3B	Rubber gloves		20
FXM000832	I-3B	Rubber gloves		0
FXM000833	I-3B	Rubber gloves		50
FXM000834	I-3B	Rubber gloves		100
FXM000835	I-3B	Cotton, overall		10
FXM000836	I-3B	Cotton, overall		30
FXM000837	I-3B	Cotton, overall		0
FXM000838	I-3B	Cotton, overall		50
FXM000839	I-3B	Cotton, overall		100
FXM000840	I-3B	Paper (For wiping)		60
FXM000841	I-3B	Paper (For wiping)		30
FXM000842	I-3B	Paper (For wiping)		0
FXM000843	I-3B	Paper (For wiping)		50
FXM000844	I-3B	Paper (For wiping)		100

* The specimen name refers to Table A-3 in Mårtensson (2015).

3 Experimental details

3.1 Investigation of colloid release

Investigation of colloid release from material specimens stored in cement water in the steel containers for about 4 years was carried out by means of Photon Cross Correlation Spectroscopy (PCCS), Section 3.1.2. The results from the analyses are presented in Section 4.1 and further discussed is Section 5.1.

3.1.1 Selected containers

Five steel containers from the laboratory scale experiments (#1, 3, 5, 9 and 19 in Table 1-1) were selected for analysis in this study. The containers were placed in a box and transported from Äspö hard rock laboratory to the laboratory at KTH[1].

3.1.2 Preparation of samples for PCCS

The valves were opened and the containers flushed with N_2 gas for 30 seconds. Thereafter samples were taken with a plastic tube connected to a syringe. The samples were taken from the top of the solution, not to disturb and generate particles physically from the different materials, Figure 3-1. After sampling the valves were again closed and the containers returned to Äspö for storage until future analyses.

The water samples were analysed for pH and for colloids (PCCS, NanoPhox, Sympatec, Germany). PCCS is based on dynamic light spectroscopy where the Brownian motion of particles in the nanometre range is monitored optically.

Figure 3-1. *Sampling of the steel containers (left image) and water samples from the steel containers (right image).*

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[1] The analyses were made at the laboratory at the division of Applied Physical Chemistry, Department of Chemistry, School of Engineering Sciences in Chemistry, KTH.

3.2 NMR study of degradation of organic materials

Investigation of degradation of different materials stored in cement buffered water in the steel containers for about 6 years was carried out by means of Nuclear Magnetic Resonance (NMR) spectroscopy. The results from the analyses are presented in Section 4.2 and further discussed is Section 5.2.

3.2.1 Selected containers

12 steel containers (#1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 17 and 19 in Table 1-1) were selected for analysis in this study. The containers were placed in a box and transported from Äspö hard rock laboratory to the laboratory at KTH[2].

3.2.2 Sample preparation

The valves were opened and the containers flushed with N_2 gas for 30 seconds. Thereafter 3–5 ml samples were taken from each cylinder using a syringe and a long needle inserted in the opened valve. The samples were taken from the top of the solution, not to disturb and generate particles physically from the different materials. After the sampling, the cylinders were flushed again with N_2 gas for 30 seconds before closing.

3.2.3 Solution state NMR studies

Structure determination

The NMR spectra were measured on a Bruker-400 DRX instrument using a 5 mm inverse probe head for ^{1}H and a 10 mm normal probe head for ^{13}C measurements. The temperature of the samples was regulated and kept constant at 25 ºC. 0.6 ml of the samples from each container was transferred to an NMR tube. The ^{1}H NMR spectra were measured without and with suppression of the very strong water signal. 10 % D_2O was added to samples from containers #1, 3, 6, 8 and 17 in which signals from degradation products were observed. The addition of D_2O is needed to stabilise the magnetic field around the sample for further NMR experiments to gain information about the structure, concentration and the approximate size (diffusion NMR experiments) of the degradation products.

In samples from containers #3 and 17 several degradation products were identified. Some of them were found in very low concentrations; hence their structural assignment was not possible in the aqueous phase. Therefore 3 ml of the samples from containers #3 and 17 respectively were stirred with 0.8 ml deuterated chloroform at room temperature for an hour. After separating the two phases, 0.6 ml of the organic phase was transferred to an NMR tube and used for further structural and diffusion measurements. The structure assignments of the degradation products are based on one- and two dimensional spectra (diffusion data detailed below) and are in agreement with data available in spectral database[3] or literature (Dauner and Pringle 2014).

Diffusion NMR experiments

Pulsed field gradient spin-echo NMR spectroscopy (PFG NMR) method was used to measure translational diffusion coefficients of solute molecules. Diffusion experiments were performed on a Bruker-500 Avance-III HD instrument using a 5 mm inverse probe head with maximum field gradient of 53 G/cm.

Diffusion coefficients are dependent on molecular sizes. In general, spectral lines belonging to different compounds exhibit different diffusion parameters while spectral peaks from the same compound should display equal diffusion coefficients. Separation of the lines in the spectrum according to diffusion properties can help in the analysis of multi-component solutions for which conventional one and two-dimensional spectroscopic methods are not fully conclusive or ambiguous. Diffusion measurements were performed on the same samples which were used for the structural studies.

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[2] The analyses were made at the laboratory at the division of Applied Physical Chemistry, Department of Chemistry, School of Engineering Sciences in Chemistry, KTH.

[3] Biological Magnetic Resonance Data Bank: http://www.bmrb.wisc.edu/

3.2.4 Solid state NMR experiments

Solid state NMR was applied to test degradation of solid materials. Experiments were performed on a Bruker-500 Avance-III HD instrument using a 4 mm magic angle sample spinning (MAS) probe head. After removing the lid, about 100 mg of rubber sample was taken from each of containers #3 and 17, Figure 3-2.

It is worth noting that a very thin organic film was observed on the top of the aqueous phase. After closing and fixing the lid, the container was flushed for 30 min with nitrogen gas via the valves on the lid.

Rubber material was wiped with tissue, cut in small pieces and loaded in a ceramic NMR rotor of 4 mm outer diameter. Solid state ^{1}H and ^{13}C spectra were measured under the MAS conditions at rotation speed 8 kHz. Since no reference (un-degraded) rubber material was available, the samples from containers #3 and 17, characterised by different temperature of the storage, were compared against each other.

Figure 3-2. *Top view of container # 3 and the rubber pieces taken for solid state NMR measurements.*

3.3 Study of specimens from field scale concrete experiments

Investigation of degradation of different materials embedded in solid concrete for about 8 years was carried out by means ^{1}H-NMR spectroscopy and gas chromatography mass spectrometry (GC-MS). The results from the analyses are presented in Section 4.3 and further discussed is Section 5.3.

3.3.1 Specimen description

A total of 40 plastic containers, each containing about 20 grams of crushed cement were prepared according to the description presented in Section 2.2. Of these, 8 containers containing crushed cement from the positions of the different organic materials were selected for analyses. Based on the results from these analyses, also containers containing cement from other parts of the original core containing rubber gloves were selected for further analyses, Table 3-1.

Table 3-1. Specimen description.

Specimen ID	Concrete Cylinder	Material type	Specimen name**	Distance from sample (mm)
FXM000807	I-2B	Ion exchange resin, sulphonate	SA3 and SA4	0
FXM000812	I-2B	Filter aid UP2	UP2a3 and UP2a4	0
FXM000817	I-2B	Ion exchange resin, anion	SB2 and SB3	0
FXM000822	I-2B	Ion exchange resin, carboxylate	WA3 and WA4	0
FXM000827	I-3B	Plastic bags, blue and transparent		0
FXM000832	I-3B	Rubber gloves, blue		0
FXM000830*	I-3B	Rubber gloves, blue		10
FXM000831*	I-3B	Rubber gloves, blue		20
FXM000833*	I-3B	Rubber gloves, blue		50
FXM000834*	I-3B	Rubber gloves, blue		100
FXM000837	I-3B	Cotton, overall		0
FXM000842	I-3B	Paper for wiping		0

* These Specimens were studied only by ^{1}H-NMR spectroscopy.
** Specimen name refers to Table A-3 in Mårtensson (2015).

3.3.2 Experimental methods and sample preparation

The analyses were performed at KTH[4] using two experimental techniques, ^{1}H-NMR spectroscopy and gas chromatography mass spectrometry (GC-MS) as detailed below.

^{1}H-NMR investigations in solution-state

^{1}H-NMR experiments

The possible organic compounds in the crushed samples were extracted with a both a polar (deuterium-oxide, D_2O, Aldrich, 99.9 atom % D) and an apolar (deuterio-chloroform, $CDCl_3$, Aldrich, 99.8 atom % D) solvent. The use of deuterated solvents is needed to avoid the very intensive proton signal from the non-deuterated solvent and to stabilise the magnetic field around the sample during the NMR experiments (by using the deuterium signal from the solvent as lock-signal). The NMR spectra were measured on a Bruker-400 DRX instrument using a 5 mm inverse probe head. The temperature of the samples was regulated and kept constant at 25 °C during the experiments.

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[4] The analyses were made at the laboratory at the division of Applied Physical Chemistry, Department of Chemistry, School of Engineering Sciences in Chemistry, KTH.

Sample preparation

Approximately 1 gram of solid sample was placed in 2 ml of deuterium-oxide, D_2O (Figure 3-3) or in 1 ml deuterio-chloroform, $CDCl_3$ (Figure 3-4) respectively. The volume of the solvents were enough to fully cover the solid sample. The samples were then ultrasonicated for 5–6 hours at room temperature. After that, the liquid and the solid phases of the samples were separated by centrifugation. The pH of the aqueous solutions was controlled by pH-indicator paper and were higher than 12. Then 0.6 ml filtrates were transferred to 5 mm NMR tubes for NMR analysis. The experimental details for each sample are shown in Table 3-2.

Table 3-2. Experimental details of the samples studied by ^{1}H-NMR spectroscopy.

Specimen ID	Distance from material specimen (mm)	NMR samples	Mass (g)	Solvent (ml)	^{1}H-NMR files		
					*NS = 32**	*NS = 32**	*NS = 128**
FXM000807	0	807-A	0.9879	D_2O (2 ml)	SKB2/11		
FXM000812	0	812-A	1.0162	D_2O (2 ml)	SKB2/12		
FXM000817	0	817-A	1.0178	D_2O (2 ml)	SKB2/13		
FXM000822	0	822-A	1.0128	D_2O (2 ml)	SKB2/14		
FXM000827	0	827-A	0.9984	D_2O (2 ml)	SKB2/15		
FXM000832	0	832-A	1.0257	D_2O (2 ml)	SKB2/16	SKB2/162	SKB2/1621
FXM000830	10	830-A	1.0253	D_2O (2 ml)		SKB2/160	SKB2/1601
FXM000831	20	831-A	1.0439	D_2O (2 ml)		SKB2/161	SKB2/1611
FXM000833	50	833-A	1.0001	D_2O (2 ml)		SKB2/163	
FXM000834	100	834-A	0.9999	D_2O (2 ml)		SKB2/164	
FXM000837	0	837-A	1.0058	D_2O (2 ml)	SKB2/17		
FXM000842	0	842-A	0.9797	D_2O (2 ml)	SKB2/18		
FXM000807	0	807-B	0.9791	$CDCl_3$ (1 ml)	SKB2/1		
FXM000812	0	812-B	1.0130	$CDCl_3$ (1 ml)	SKB2/2		
FXM000817	0	817-B	1.0000	$CDCl_3$ (1 ml)	SKB2/3		
FXM000822	0	822-B	1.0225	$CDCl_3$ (1 ml)	SKB2/4		
FXM000827	0	827-B	1.0025	$CDCl_3$ (1 ml)	SKB2/5		
FXM000832	0	832-B	1.0179	$CDCl_3$ (1 ml)	SKB2/6		
FXM000837	0	837-B	1.0366	$CDCl_3$ (1 ml)	SKB2/7		
FXM000842	0	842-B	0.9900	$CDCl_3$ (1 ml)	SKB2/8		

(*NS = number of scans recorded.*)

Figure 3-3. *Samples in of deuterium-oxide before ultrasonification.*

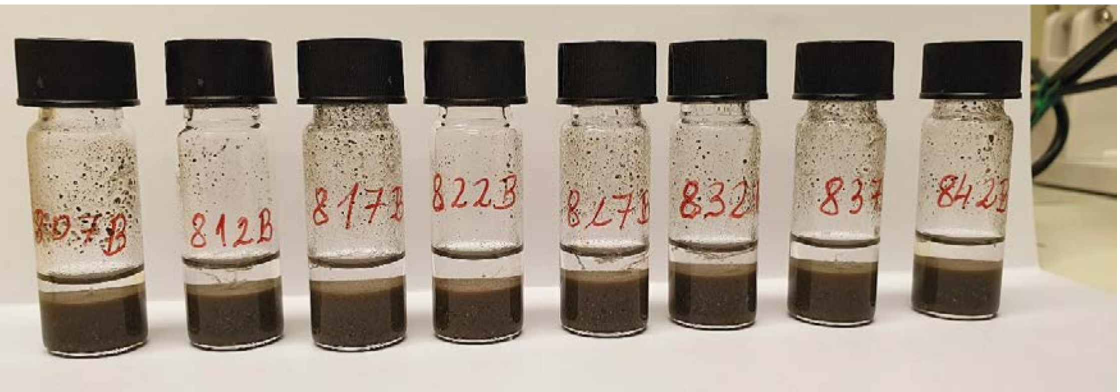

Figure 3-4. Samples in deuterio-chloroform before ultrasonification.

Analysis using gas chromatography-mass spectrometry (GC-MS)

The samples from the cement cylinders were analysed with GC-MS following sample treatment performed in different ways. All samples were extracted using ultrasonication but the way of preparing for injection and the actual injection differed. The samples and corresponding sample treatments are listed in Table 3-3. Here, all samples came from the part of the original cement core which contained the original material specimen.

Table 3-3. Samples analysed with GC-MS using LI and SPME respectively. All samples were prepared with Ultrasonic Assisted Extraction.

Sample Name	Sample preparation method	Solvent (5 mL)	Mass (g)
FXM000807	UAE/LI	MeCN	1.0006
FXM000812	UAE/LI	MeCN	1.0017
FXM000817	UAE/LI	MeCN	1.0019
FXM000822	UAE/LI	MeCN	1.0017
FXM000827	UAE/LI	MeCN	1.0018
FXM000832	UAE/LI	MeCN/MeOH	1.001
FXM000837	UAE/LI	MeCN	1.0019
FXM000842	UAE/LI	MeCN	1.0013
FXM000807	UAE/SPME	Water*	1.0026
FXM000812	UAE/SPME	Water*	1.007
FXM000817	UAE/SPME	Water*	1.0018
FXM000822	UAE/SPME	Water*	1.0033
FXM000827	UAE/SPME	Water*	1.0011
FXM000832	UAE/SPME	Water*	1.001
FXM000837	UAE/SPME	Water*	1.001
FXM000842	UAE/SPME	Water*	1.0018

** Doubly distilled water with a resistivity of 18.2 MΩ × cm at 25 °C.*
UAE – Ultrasonic Assisted Extraction, LI – Liquid Injection, SPME – Solid-Phase Micro Extraction.

Ultrasonic extraction

Crushed material was mixed with 5 mL of GC-MS grade acetonitrile (CH_3CN) or doubly-distilled water according to the information shown in Table 3-3. The volume of the solvent was chosen to be large enough to fully cover the solid sample. The samples were then ultrasonicated for 60 minutes. The acetonitrile samples were filtrated through a 25 mm polypropylene membrane filter with a pore size of 0.2 µm before automatic injection into GC-MS. The reason for this was to avoid any particles entering the column of the GC as the acetonitrile samples were analysed with liquid injection. The filtration step was not necessary for the water samples since they were not injected directly into the GC-MS instrument. For each sample, one extraction was performed with two injections analysed for each sample. Sample FXM000832 was extracted three times with both solvents, with two injections performed per extraction as this sample was chosen to be used for the validation of the liquid injection method. Based on these results, which showed more peaks in a wider time range using acetonitrile (Figure C-6), this solvent was chosen as the more suitable extraction solvent for the remaining samples.

Solid phase micro extraction (SPME)

Following UAE, the water samples were subjected to SPME collection to avoid injecting water into the GC-MS instrument and also to explore the more volatile constituents of the samples. A DVB/PDMS (divinylbensene/polydimethylsiloxane) 24 gauge SPME fibre was placed in the headspace (gas phase) of the water samples for 30 minutes. This type of fibre is nonpolar so that mainly nonpolar analytes are absorbed. After the collection the SPME fibres were inserted into the GC injector and the samples were injected manually by desorbing for 10 seconds. Each sample was extracted two separate times with one injection each. Sample FXM000832 was extracted three times with three injections performed per extraction as this sample was chosen to be used for the validation of the SPME method.

GC-MS analysis

All the samples were analysed with GC-MS (Agilent Technologies 7890A GC system and 5975C inert MSD) using a 30 m DB-5 capillary column with a 0.25 mm diameter and a 0.25 µm film thickness. The mass spectrometer uses electron impact as ionisation source, a single quadrupole as mass analyser and a triple axis detector.

A temperature program was used to optimise the chromatographic resolution. The initial temperature was 40 °C, which was held for 1 minute. The temperature was then increased to 260 °C at a rate of 10 °C/min and held at 260 °C for 5 minutes. The total time of the analysis method was 28 minutes. The injection system heating program was as follows: after 0.1 minute the system was heated to 260 °C at a rate of 12 °C/min and then held for 2 minutes. This heating program was used in order to get narrow injection bands resulting in better chromatography efficiency.

Every sample was run two times and blanks only containing acetonitrile were analysed to record background and distinguish possible contaminants. For the SPME analysis, blanks were run by performing an injection with the SPME fibre as described above but without exposing the fibre to the sample headspace prior to the injection. This was done prior to the first headspace collection of the sample to generate the blank and between each run in order to prevent any carry-over between the SPME analyses.

Data collected from each sample includes retention times and mass spectra. Retention times were used in combination with a C7-C40 alkane standard to calculate the analytes' retention time index (RI). The RI can be used for analyte identification by comparing the calculated values with reference values from the National Institute of Standard and Technology (NIST) database library[5]. The RI values were calculated according to the Van den Dool and Kratz formula for RI values obtained from temperature ramp analysed GC data. This comparison was done to verify identification obtained from the MS database search results.

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[5] The MS reference database used for the evaluation of the GC-MS data was the NIST MS Search 2.0 program for the NIST/EPA/NIH Mass Spectral Library version 2.0 g, build 2009.

4 Results

4.1 Investigation of colloid release

The pH in all the water samples from the steel containers was somewhat lower than expected, Table 4-1. The pH measurement was performed without bubbling N_2 (gas) so most likely CO_2 (g) has dissolved into the water during the measurement causing a decrease in the pH. The pH in the water in the steel containers is therefore probably higher.

Table 4-1. pH in the samples from the different steel containers.

Sample from container #	pH
1	9.1
3	9.6
5	-
9	10
19 (Reference)	10

The presence of colloids in the different solutions was studied by means of PCCS. The PCCS signals were in the order of 5–11 kcps in the containers containing different types of organic materials and somewhat lower in the reference container (#19) which only contained crushed cement paste and no organic material (Table 4-2). According to experience, the particle concentration found in these containers are similar to what is typically found in ordinary tap water and the conclusion is thus that no additional colloids have been formed through degradation of the organic materials in the containers.

It should be noted that the signal is unstable if the concentration of colloids is very low as was the case for all samples in this study. Since no particles were detected in the solution no further analysis were performed on these specimens.

Table 4-2. PCCS signal from the samples from the different steel containers.

Sample from container #	PCCS signal (kcps)
1	9
3	7
5	11
9	6
19 (Reference)	3

4.2 NMR study of degradation of organic materials

4.2.1 pH

pH for samples from some of the steel containers (measured using a combined glass electrode in air) is presented in Table 4.3. A comparison with the pH of the solutions presented in Table 4-1 show that pH in the containers in this study are clearly higher than in the previous study.

Table 4.3. pH in the samples from the different steel containers.

Sample from container #	pH
1	12.2
3	11.5
6	12.4
8	11.5
17	11.6

4.2.2 Solution state NMR

The ^{1}H NMR spectra measured with and without suppression of the water signal are shown in Figures B1 to B12. The water suppressed ^{1}H NMR spectra of samples from containers #1, 3, 6, 8 and 17 showed some additional signals in comparison to the reference sample (container #19) due to a certain degree of decomposition of the material specimens in these containers. The signals from the products in the corresponding spectra are marked with red squares in Figures B1 to B12.

The intensities of the ^{1}H signals observed in samples from containers #1, 6 and 8 (see Table 1-1 for details) are very similar. The signal intensities relative to the signal intensity of the internal reference (TSP-d_4) added to the each samples in 3.5 mM concentration indicates that the concentrations of the degradation products are in the same range, Figure B-13. These spectra were obtained using the same experimental conditions; hence the relative intensities of the signals can be compared between the samples too. For these samples no structural assignments were possible due to low concentration of the compounds formed and mostly due to the singlet structure of the peaks. The diffusion data presented in Figure 4-1, clearly suggest the formation of a number of different small molecules.

The ^{1}H NMR spectra of samples from containers #3 and 17 showed very strong signals from various compounds indicating a significant degree of dissolution and hydrolysis of some rubber additives (plasticisers and/or softeners). The ^{1}H NMR spectra shown in Figure B-14 from samples from containers #3 and 17 are measured using the same experimental conditions and setup. The two spectra are practically identical – the fine structure of the signals and their intensities are the same – demonstrating a similar degree of decomposition of the additives (independently from the storage temperature). The identified compounds, their concentrations in the containers #3 and 17 and diffusion coefficients are given in Table 4-4. The ^{1}H and ^{13}C spectra with the signal assignments of the products are shown in Figures 4-2, 4-3 and 4-4.

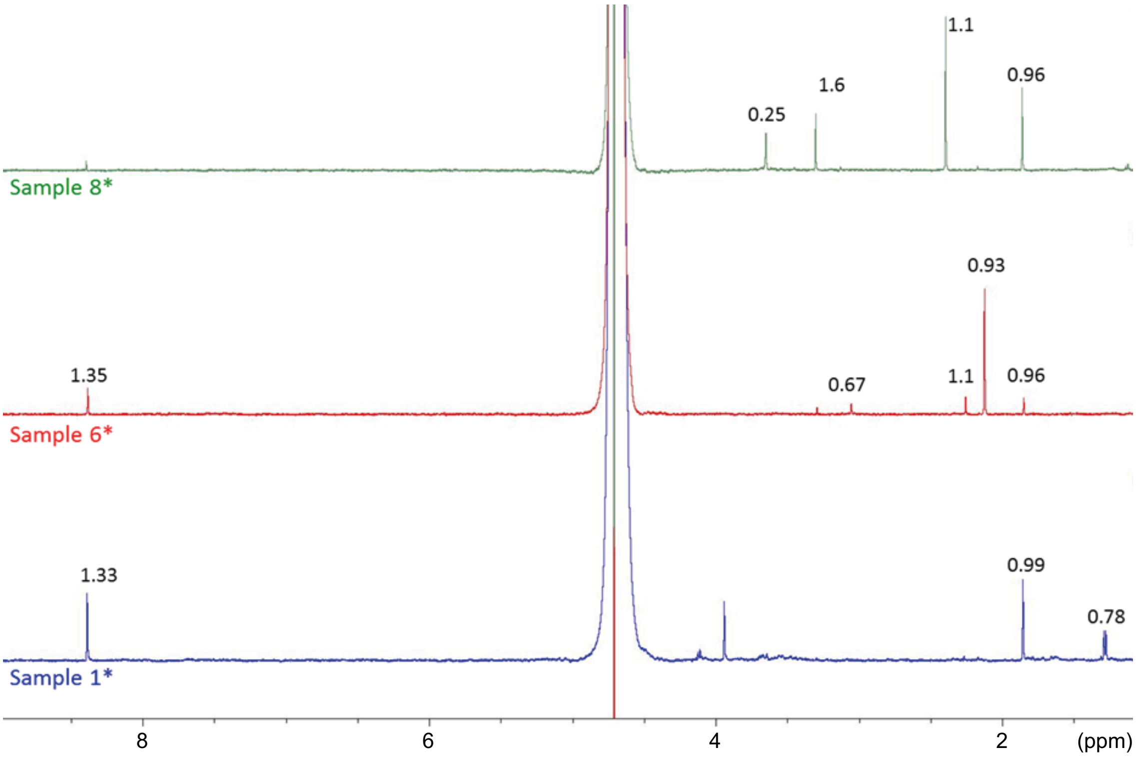
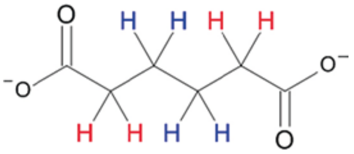
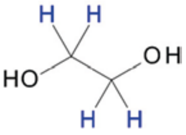
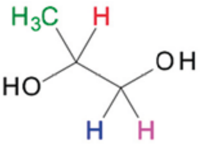
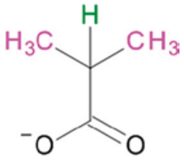
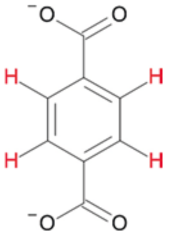
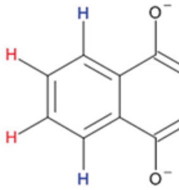
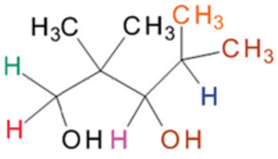


Figure 4-1. *^{1}H NMR signals recorded with water pre-saturation in samples from containers #1, 6, and 8 (from bottom to top) and the measured diffusion coefficients (10^{-9} m^2/s).*

Table 4-4. Structures, concentrations and diffusion coefficients for the molecules identified in steel containers #3 and 17.

Compound #	Name	Structure	Concentration in the container (mM)	Diffusion coefficient (10^{-9} m^2/s)
1	Adipic acid (Ca^{2+}-salt)		16	0.58
2	Ethylene glycol		5	1.1
3	1,2-Propylene glycol		4.8	0.79
4	Isobutyric acid (Ca^{2+}-salt)		3.2	0.78
5	Terephthalic acid (Ca^{2+}-salt)		1.6	0.64
6	Phthalic acid (Ca^{2+}-salt)		1.4	0.69
7	2,2,4-Trimethyl-1,3-pentanediol (from extraction with $CDCl_3$)		1.6	1.68 (in $CDCl_3$)

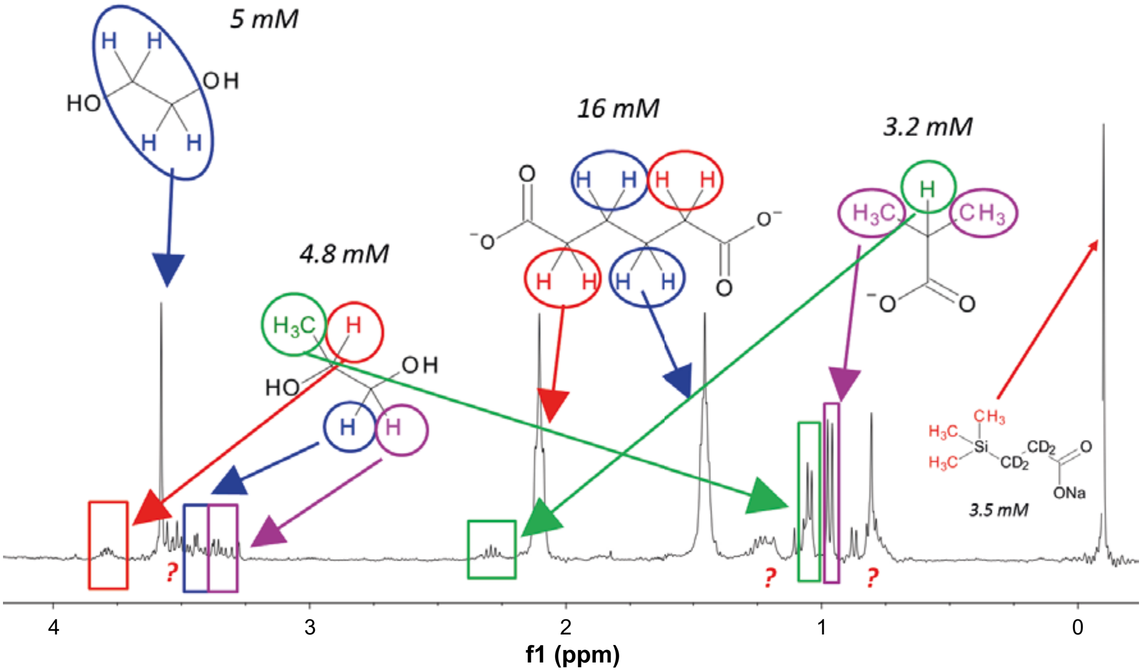


Figure 4-2. *Aliphatic region of the* ^{1}*H NMR spectrum of container # 3 showing the signal assignments of the products. The intensities of signals with question marks were not high enough for structure determination in the aqueous phase. These signals are from compound # 7 (Table 4-4.) as was determined in the* $CDCl_3$ *phase from extraction experiments (see text for details).*

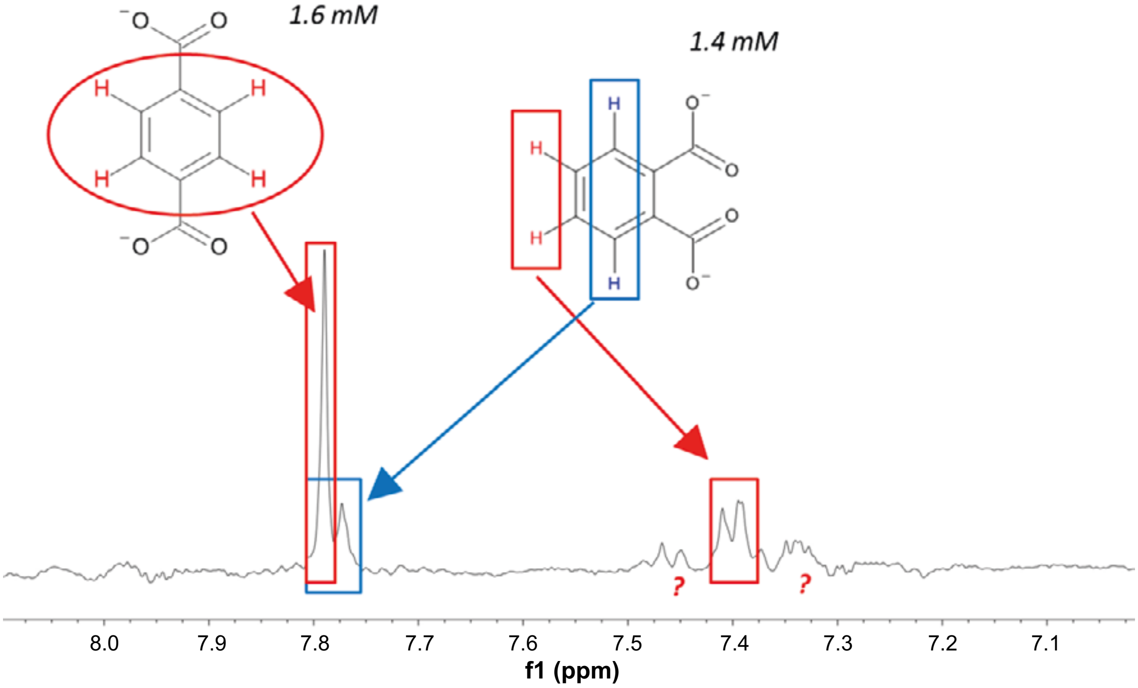


Figure 4-3. *Aromatic region of the* ^{1}*H NMR spectrum of container # 3 showing the signal assignments of the products. The intensities of the signals with question marks were not high enough for structure determination.*

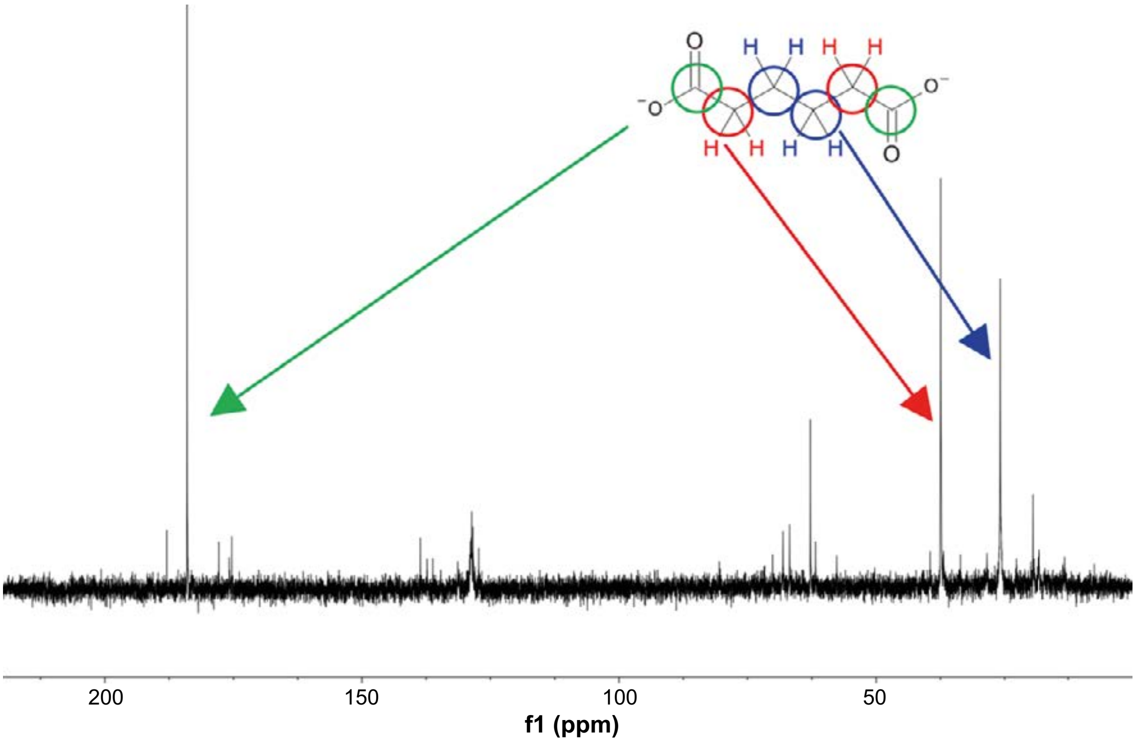


Figure 4-4. *^{1}H decoupled ^{13}C NMR spectrum of sample from container #3 with the signal assignments for the major product, adipic acid (Ca^{2+} salt).*

The assignments of the ^{1}H NMR signals were confirmed by a ^{1}H-^{1}H COSY spectrum (Figure B-16). The concentrations of the products of the aqueous samples in the containers were calculated from the comparison of the signal intensities (signal integrals) and the intensity (integral) of an internal reference (TSP-d_4) added to the samples (3.5 mM), as shown in Figure B-15. Diffusion data in Table 4-4 are also in accordance with the proposed structures.

The question marks in Figure 4-2 indicate signals from products for which structure determination was not possible due to the very low concentrations of these species in the aqueous phase. Due to expected higher solubility of these compounds in a less polar organic solvent, samples from containers #3 and 17 were extracted with deuterated chloroform ($CDCl_3$). The ^{1}H NMR spectra of these samples were identical as shown in Figure B-17. By addition of a few drops of D_2O to the samples, 2 OH signals disappeared from the spectra as shown in Figure B-18. Based on this observation, diffusion data, and the ^{1}H-^{1}H COSY spectrum (Figures B-19 and B-20) the product was identified as compound 7 (2,2,4-Trimethyl-1,3-pentanediol) in Table 4-4.

The assignments of the ^{1}H NMR signals of 2,2,4-Trimethyl-1,3-pentanediol are shown in Figure 4-6. Its di-isobutyrate ester is a well-known plasticiser in polymer chemistry (Wypych 2004)[6, 7] and it can therefore be assumed that the diol is formed by the hydrolysis of this ester. Its concentration, which is just half of the isobutyrate concentration, can be calculated to about 1.6 mM. The signals marked with light blue squares and question marks could arise from several compounds containing long carbon chains consisting of 10–20 carbons and their structure could not be determined. These can be halogenated paraffin, fatty acids or various oils such as palm oil used as plasticisers (or softeners) in polymer chemistry (Wypych 2004). Since their signals are missing from the spectra recorded in the aqueous samples it can be assumed that they form the very thin film of the organic phase observed on the top of the aqueous phase, Section 3.2.4.

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[6] http://www.globalspec.com/ds/3456/areaspec/function_plasticizer

[7] http://www.chemicalbook.com/ProductChemicalPropertiesCB3125652_EN.htm

The signals from the aromatic compounds (#5 and 6 in Table 4-4) and the signals labelled with question marks in Figure 4-3 are missing from the spectra recorded in $CDCl_3$ (figure not shown). It means that these compounds could not be extracted to the organic phase indicating their ionic character. Based on literature data (Wypych 2004) it is known that – in general – all the three phthalate ester (or the acids) isomers are used in rubber industry as plasticisers or softeners. Based on this it is assumed that the aromatic signals with question marks in Figure 4-3 are from the third structural isomer, that is from isophthalate (calcium salt).

Based on these results it is concluded that the identified compounds (#1–7 in Table 4-4) are formed from dissolved additives of the rubber gloves. The identified carboxylic acid derivates (calcium-salt) or alcohols (diols) are in accordance with the structures of well-known plasticisers (or softeners), adipate-, phthalate- and isobutyrate esters (Wypych 2004). The identified structures are formed by the hydrolysis of the corresponding esters, a basic reaction in carbonyl chemistry. The general mechanism of their formation, a base promoted hydrolysis of esters (Solomons et al. 2014), is shown in Figure 4-5. This is an essentially irreversible reaction since the carboxylate ion is very stable and unreactive toward further nucleophilic substitutions because it is negatively charged. This explains why the effect of the difference in storage temperature on the composition of the samples from containers #3 and 17 is negligible.

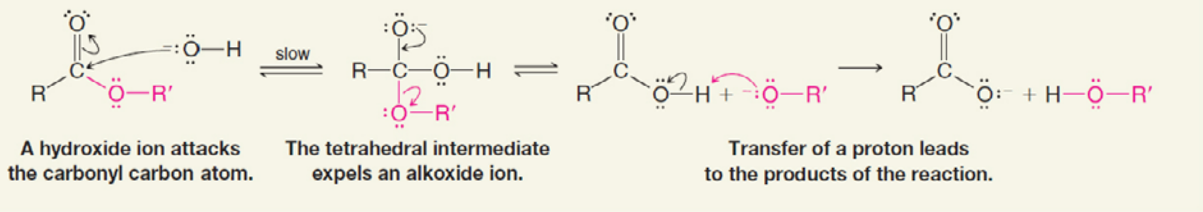


***Figure 4-5.** Mechanism of the base promoted hydrolysis of esters (Solomons et al. 2014).*

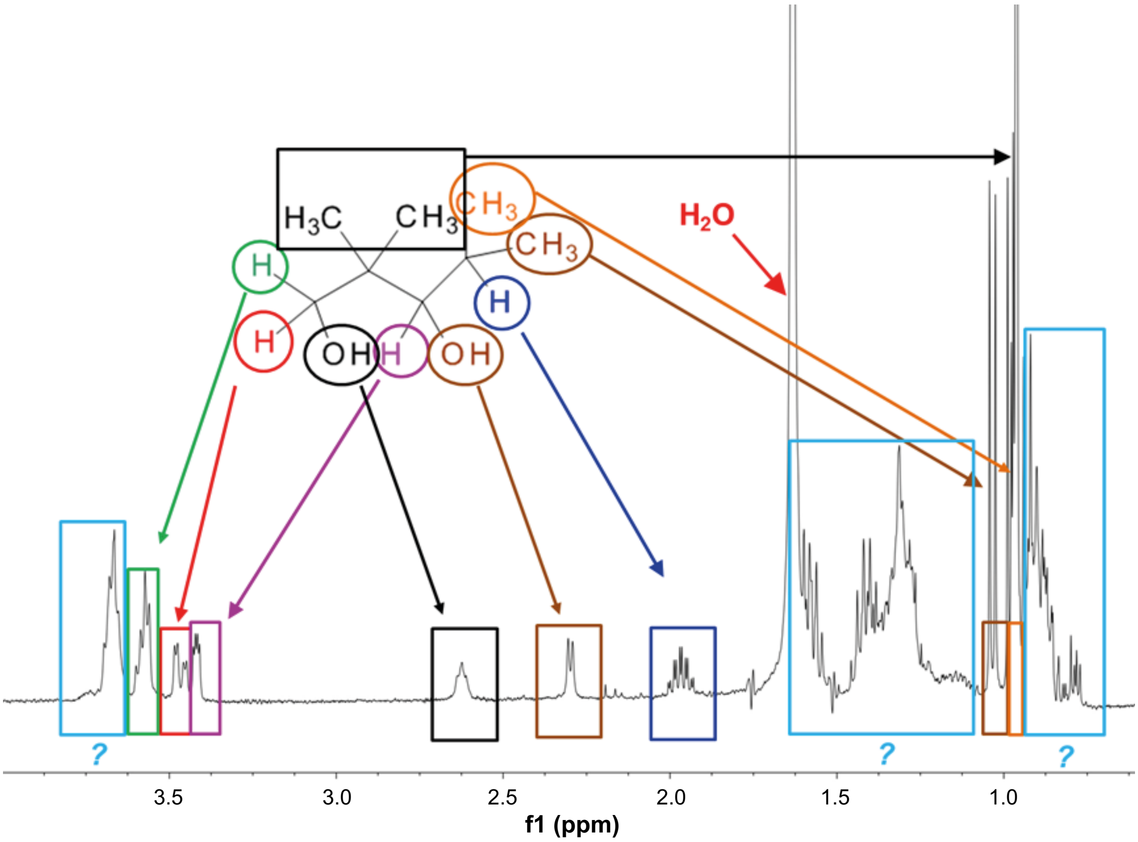


***Figure 4-6.** ^1H NMR spectrum and signal assignments of the degradation products extracted into the $CDCl_3$ phase from container # 3. The signals with question marks could arise from several compounds containing long carbon chains and their structure could not be determined (see text for details).*

It should here be noticed that calcium-adipate, being the major degradation product with a concentration of 16 mM in containers #3 and 17, contains two carboxylate groups. Being regarded as a bidentate ligand in coordination chemistry it can coordinate to actinide or lanthanide ions by both carboxylate groups and form stable chelated complexes. It can also compete with the hydroxide ion in aqueous solutions and can contribute to the dissolution and transport of metal ions in natural waters.

4.2.3 Solid state NMR

By using Solid State MAS NMR spectroscopy, it is possible to detect degradation of the solid material directly, without dissolving it in a solution. Depending on the extent of internal molecular mobility, solid materials can be classified as *rigid solids* and *soft solid*s, the latter ones exhibiting some significant degree of motion of constituting molecules or molecular parts. By applying different solid state NMR techniques one can distinguish between rigid and soft solid components in a sample. For example, with ^{13}C Cross-Polarisation (CP) method one detects almost exclusively the signals of immobilised molecules (rigid component). While in the experiment with 90° excitation pulse, the signals of both, rigid and soft, components are recorded. Moreover, rigid component typically exhibits broader, less resolved, spectral lines.

Analysis of ^{13}C spectra obtained from NMR studies of the solid specimens in containers #3 and 17 revealed the presence of two components with different molecular rigidity. One of the components gave rise to broad lines characteristic of rigid polymers while the second component contributed with relatively narrow lines indicative of the presence of softer rubber-like material and/or plasticiser additives. The spectral shapes of the two samples are essentially similar except the different relative contributions of "rigid" and "soft" components, which is simply due to different amounts of the corresponding parts in the taken material pieces. Likewise, ^{1}H MAS spectra of two samples display comparable structures. This suggests that the degradation degree, if any, is similar in containers #3 and 17 despite the difference of the storage temperature. This conclusion is in agreement with the results of the NMR analysis of solution samples. The spectra are shown in Figures 4-7, 4-8 and 4-9.

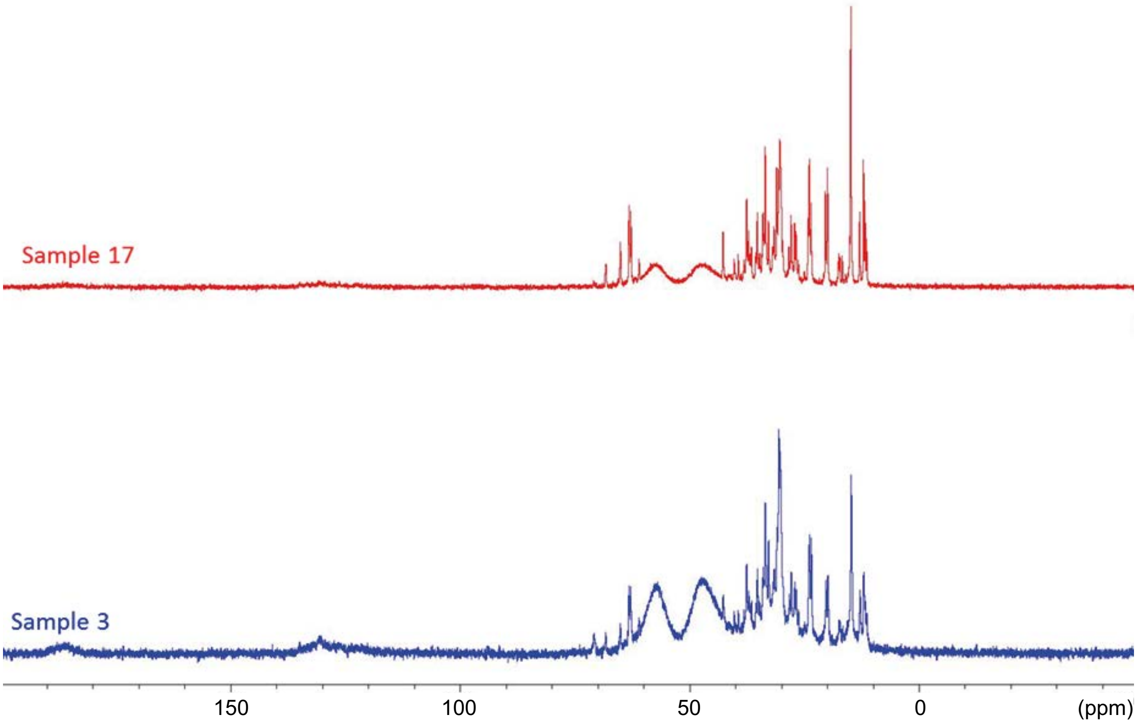


Figure 4-7. *125 MHz ^{13}C solid state MAS NMR spectra of solid materials from containers # 3 and 17 recorded at spinning speed 8 kHz.*

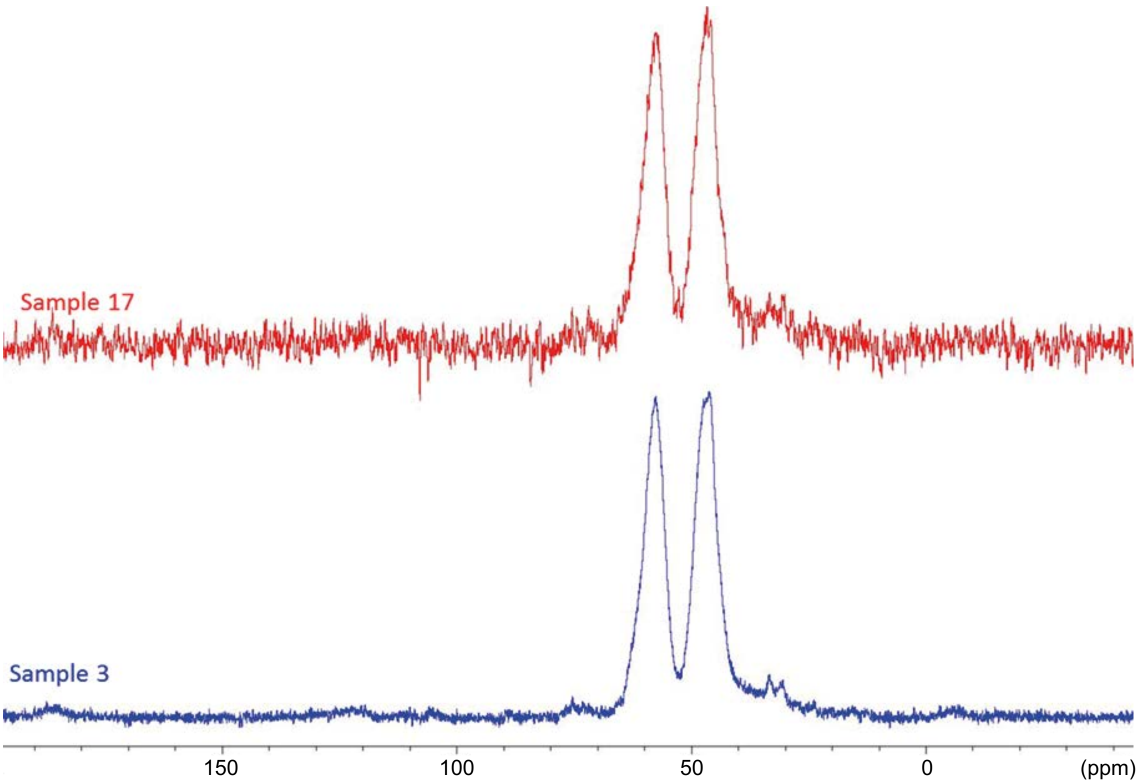


Figure 4-8. *125 MHz ^{13}C solid state CP-MAS NMR spectra of solid materials from containers # 3 and 17, recorded at spinning speed 8 kHz. In CP (cross-polarisation) spectra only signals of relatively rigid molecules or molecular parts are observed.*

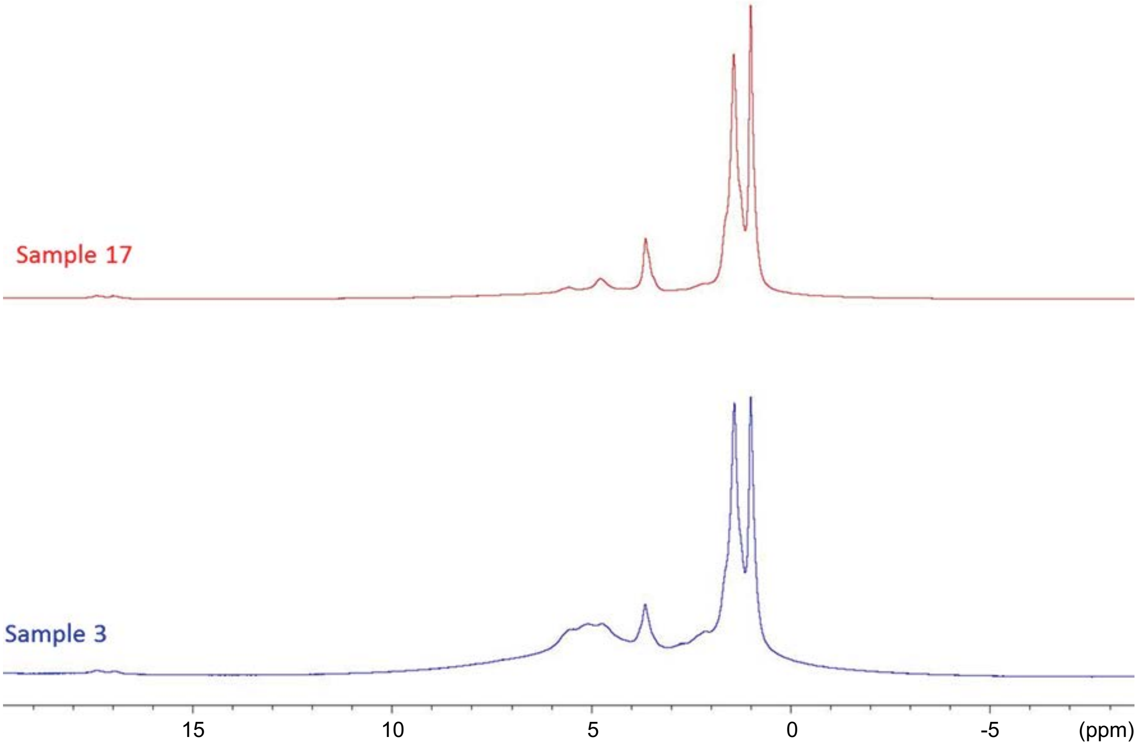


Figure 4-9. *500 MHz ^{1}H solid state MAS NMR spectra of the original solid specimens in containers # 3 and 17, recorded at spinning speed 8 kHz.*

4.3 Study of specimens from field scale concrete experiments

4.3.1 ^{1}H-NMR investigations

The structure assignment of the released organic compounds is based on the comparison between the NMR spectra obtained in this study and those reported in Section 4.2.

Extraction with deuterio-chloroform

The stacked plot of the ^{1}H-NMR spectra from specimens corresponding to the positions of the material specimens in the concrete cylinders are shown in Figure C-1. The spectra are practically identical (apart from specimen 832B, corresponding to FXM000832 in Table 3-2) and show signals only from the non-deuterated solvent residual peak ($CHCl_3$) at ca 7.2 ppm, and from some aliphatic compounds in the range of 0.5–1.5 ppm which are presumably originating from cement additives. The spectrum of specimen FXM000832 (containing pieces of a rubber glove) show some extra signals marked with the red circle in Figure C-1. We assume that these signals are from 2,2,4-trimethyl-1,3-pentanediol (Compound #8 in Table 4-5) as identified earlier as one of the additives in rubber gloves shown in Figure 4-2.

It must be recognised that even though the intensity of these signals are close to the detection limit of ^{1}H-NMR they can nevertheless be used to calculate the relative concentration of this compound. We know that the integral of the very intensive residual signal of $CHCl_3$ at 7.2 ppm represent ca 0.2 atom % hydrogen content in the solvent (99.8 % $CDCl_3$ from Aldrich). From this the $CHCl_3$ concentration of ca 0.01 M can be calculated and can be used as an internal reference. The relative integral for all signals from 2,2,4-trimethyl-1,3-pentanediol is 1, while the integral for the $CHCl_3$ signal is ca 850. Hence, 2,2,4-trimethyl-1,3-pentanediol contains 18 protons, the relative integral for one proton is 0.055. From these the concentration of 2,2,4-trimethyl-1,3-pentanediol in the extracted sample is approximately $(0.055/850) \times 0.01 = 6.5 \times 10^{-7}$ M.

Extraction with deuterium-oxide

The stacked plot of the ^{1}H-NMR spectra from specimens corresponding to the positions of the material specimens in the concrete cylinders are shown in Figure C-2. The spectrum of specimen FXM000832 (with pieces of a rubber glove) differs from the other spectra and show signals from organic materials. Beside this, one can clearly see that the spectra of the four samples from concrete cylinder I-2B are practically identical but differ from the samples from concrete cylinder I-3B. The relatively intensive signals marked with a red rectangle at 3.51 ppm show that these samples contain ethylene glycol ($HO\text{-}CH_2\text{-}CH_2\text{-}OH$). The presence of this compound is explained by the fact that ethylene glycol was used in the preparation of the cement specimens containing ion exchange resins and filter aid which were placed in concrete cylinder I-2B (Mårtensson 2015). Figure 2-9 (left image) shows a specimen of which the right half represents the cement specimen containing filter aid and the left part the concrete cylinder. No ethylene glycol was added to the main concrete cylinder, hence no ethylene glycol was found in the specimens from concrete cylinder I-3B.

Since the spectrum from specimen FXM000832 (with pieces of a rubber glove) showed a significant degree of release of organic compounds four other samples obtained at a distance of 10, 20, 50 and 100 mm from the rubber glove respectively were investigated by NMR spectroscopy. The NMR spectra shown in Figure C-3 show that the same signals with the same intensities are found in the sample obtained 10 mm from the rubber glove as in the specimen where the rubber glove was initially placed, indicating significant transport of the organic materials in the solid concrete. The spectra from samples obtained 20, 50 and 100 mm from the pieces of rubber gloves are more or less similar and do not show any organic signals. Figure C-4 shows a comparison of the spectrum of specimen FXM000832 (with pieces of a rubber glove) and the spectrum from the steel containers containing the same type of rubber glove shown in Figure B-14. Based on the comparison of the spectra it is concluded that the same molecules have been released from samples in water and samples embedded in solid concrete as listed in Table 4-5.

Figure C-5 shows the signal assignments in the aliphatic spectral region (between 0.5–4.0 ppm) made as a part of the study presented in Section 4-2. However, differences can be observed in the signals appearing in the aromatic region, i.e. in the area 7.0–8.5 ppm in Figure C-4. In the work presented in Section 4-2 di-substituted carboxylic acids (phthalic and terephthalic acid) were found to be the dominating aromatic degradation products.

However, the relative integral ratio of 2:1:2 of the aromatic signals in the spectrum of specimen FXM000832 indicates that the major degradation product must be a mono-substituted aromatic compound. As it was assumed that this compound was a benzoic acid derivative, a reference spectrum of sodium-benzoate in D_2O was recorded. The comparison of the two spectra shown in Figure 4-10 confirmed that the major aromatic compound in sample FXM000832 must be the calcium salt of benzoic acid (compound #7 in Table 4-5). Note that the slight differences observed in the chemical shifts must be due to the different metal-ions and differences in concentrations and/or pH.

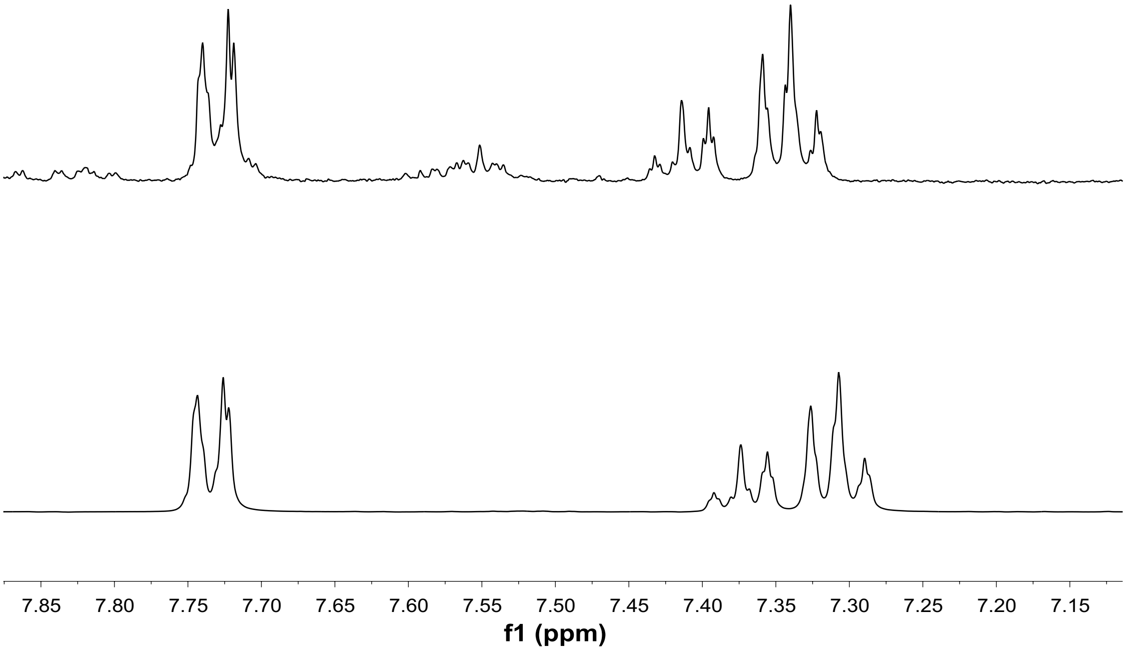
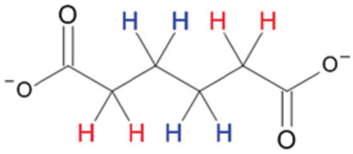
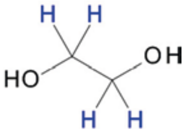
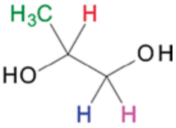
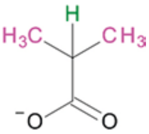
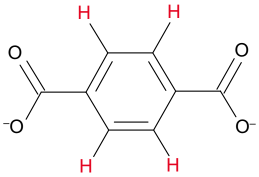
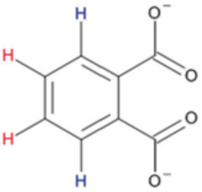
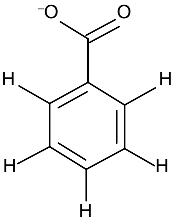
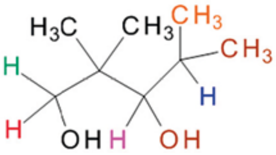


Figure 4-10. *Aromatic region of the* ^{1}*H-NMR spectrum of specimen FXM000832 containing pieces of a rubber glove (top) and sodium-benzoate (benzoate) in* D_2O *(bottom).*

Table 4-5. Structures of the organic molecules identified in samples FXM000832 and FXM000830.

Compound #	Name	Structure
1	Adipic acid (Ca^{2+}-salt)	
2	Ethylene glycol	
3	1,2-Propylene glycol	
4	Isobutyric acid (Ca^{2+}-salt)	
5	Terephthalic acid (Ca^{2+}-salt)	
6	Phthalic acid (Ca^{2+}-salt)	
7	Benzoic acid (Ca^{2+}-salt)	
8	2,2,4-Trimethyl-1,3-pentanediol (from extraction with $CDCl_3$)	

4.3.2 Analysis using gas chromatography-mass spectrometry (GC-MS)

Liquid injection

The chromatograms obtained from injection of the acetonitrile samples only contained a few significant peaks (Figure C-7). These were identified with MS (not RI) as cyclododecane and lauryl acrylate.

Solid phase micro extraction (SPME)

The samples prepared and injected using Solid Phase Micro Extraction (SPME) gave more complex chromatograms and more identified substances correspondingly. A number of reoccurring peaks could be distinguished in all these chromatograms albeit with varying intensities (Figure C-8).

The more abundant peaks were identified with MS and RI. Figure C-9 and Table C-1 show the chromatogram and identified substances from sample FXM00807. The only sample that showed peaks others than these reoccurring ones was FXM000832 containing pieces from a rubber glove (Figure 4-11). The peaks which were unique for this sample were also identified with both MS and using RI (Figure 4-11 and Table 4-6).

However, as shown in Table C-1 related to the analysis of FXM000807, some compound names are repeated in the lists. This is because the determined RI values are not available for the same GC-MS instrumentation as the one used in this study. Furthermore, the mass spectra of this type of substances look similar; the difference between the compounds can simply be the position of for example a methyl group. Some compounds have been matched with theoretical RI values, thus there can be some variance in the value observed in the present study in relation to that of the reference value. The RI values are here used to avoid false positive identification.

In order to determine the origin of the compounds detected with certainty, a list of compounds such as grinding aids used in cement production would allow for the sorting of which compounds belong to the background and what compounds belong to the material placed within each core. However, since there are several compounds that reoccur across most of the samples, it could be assumed that these originate from additives used in cement production from which the concrete was made.

Table 4-6. Peaks identified in chromatogram from sample FXM000832.

Ret Time	CAS Number	Name	RI	RI ref
7.767	17302-28-2	2,6-Dimethylnonane[a]	1013	1025
8.114	104-76-7	2-Ethylhexanol	1032	1028
9.634	33933-80-1	1-Nonanol, 4,8-dimethyl-	1137	1229
8.445	3452-97-9	1-Hexanol, 3,5,5-trimethyl-	1052	1049
9.927	6976-28-9	1-Methylpentyl cyclopropane	1139	-
11.85	1014-60-4	Bensene, 1,3-bis(1,1-dimethylethyl)-	1260	1245
14.08	112-54-9	Dodecanal	1410	1407

Ret Time: Retention time, RI: Retention index, RI ref: Reference retention index. [a)] This peak also reoccurred in all chromatograms.

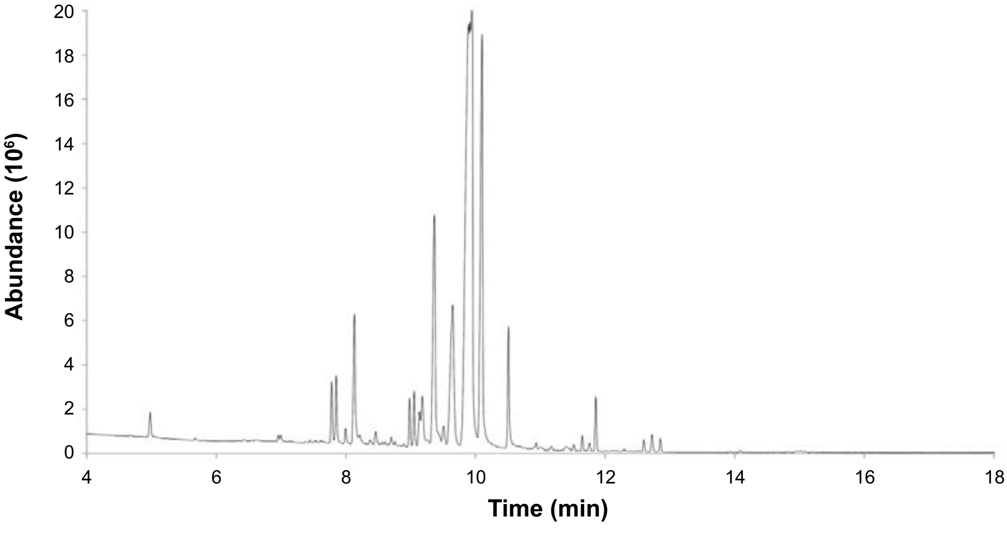


Figure 4-11. *Chromatogram from sample FXM000832.*

5 Summary and conclusions

In this report, the results from 3 different studies on degradation of different types of organic materials in cementitious environments and transport of the degradation products in solid concrete have been presented. The overall conclusions from these studies which are summarised in Sections 5.1 to 5.3 are that degradation has been very limited. The study showed that only in the steel containers containing rubber gloves degradation products could be found in a high enough concentration for identification of the chemical compounds to be possible. The molecules found in these containers could be identified as originating from well-known softeners/plasticisers used in the plastic industry.

5.1 Colloid release from organic materials

The amount of colloids found in the steel containers containing different types of organic material was on the same level as in ordinary tap water. The conclusion is therefore that no colloids have been formed through degradation of the organic material within these containers. This is in accordance with current theory that states that the formation of colloids is suppressed in waters of high ionic strength.

5.2 NMR study of degradation of organic materials

The NMR spectra of samples from containers #1 (Cotton), 6 (Ion exchange resin) and 8 (Filter aid) showed signals indicating only minute degradation of the material. In these samples no structural assignments were possible due to low concentration of the compounds formed (in the micro molar range) and mostly due to the singlet structure of the peaks. The diffusion data, however clearly suggest the formation of a number of different small molecules. Because of their very low concentration it is assumed that complex formation with radioactive actinide or lanthanide isotopes in the pH range of the test solutions (11–12) is negligible and cannot contribute to migration of these isotopes in a cementitious environment.

In steel containers #3 and 17 (Both containing pieces of rubber gloves) several different organic compounds were identified. Beside the compounds listed in Table 4-4 it is also assumed that calcium-isophthalate and one (or more) products containing long aliphatic carbon chains (C_{10}–C_{20}) are either formed or only dissolved from the rubber. The NMR spectra from samples from these containers are practically identical and show signals from the same compounds which indicate that difference in the storage temperature have had no effect on the routes of degradation of the rubber gloves.

Solid state NMR measurements show that the remaining solid rubber polymers are the same in the two containers. The identified compounds shown in Table 4-4 are formed by hydrolytic reaction of the dissolved additives of rubber. The identified carboxylic acid derivates (calcium-salt) or alcohols (diols) are in accordance with the structures of well-known plasticisers (or softeners), adipate-, phthalate- and isobutyrate esters used in rubber industry (Wypych 2004).

However, calcium-adipate, being the major degradation product with a concentration of 16 mM in containers #3 and 17, contains two carboxylate groups. Being regarded as a bidentate ligand in coordination chemistry it can coordinate to actinide or lanthanide ions by both carboxylate groups and form stable chelated complexes. It can also compete with the hydroxide ion in aqueous solutions and can contribute to the dissolution and transport of metal ions in natural waters.

5.3 Study of specimens from field scale concrete experiments

Among the specimens studied in this work, NMR analyses could only detect organic degradation products in samples from specimens FXM000832 and FXM000830 which both were extracted from a concrete core containing pieces of the same type of rubber gloves as discussed in Section 5-2. For the other specimens no organic compounds other than those supposedly identified as originating from the cement additives (e.g. grinding aid used during cement production) could be found. The NMR spectra from samples obtained by aqueous extraction of specimens FXM000832 and FXM000830 were practically identical. As FXM000830 was obtained at a distance of about 10 mm from the pieces of rubber gloves in the cement cylinder, this indicates that diffusion of the identified organic materials in concrete has occurred. No degradation products from the rubber gloves were identified in spectra from specimens at a distance from 20 mm and above implying that diffusion has been limited to the region very close to the pieces of the rubber glove.

In the NMR spectra from samples FXM000832 and FXM000830 signals from the same compounds as those identified in the study summarised in Section 5-2 were found. The only difference is that the formation of benzoic acid (or its calcium salt) has occurred to a larger extent in the cement cylinder, probably via decarboxylation of the phthalates.

The identified carboxylic acid derivates (calcium-salt) or alcohols (diols) are in accordance with the structures of adipate-, phthalate- and isobutyrate esters which are well-known plasticisers (or softeners), used in rubber industry. Of the identified compounds only the adipic and phthalic acids as bidentate ligands can compete with the hydroxide ion in aqueous systems. By coordination of both carboxylate groups stable chelate complexes can be formed which can contribute to the dissolution and transport of metal ions in natural waters.

Studies by means of GC-MS analysis using SPME and UAE confirmed the findings in the NMR studies that the most abundant compounds detected are aliphatic compounds. As in the NMR studies, sample FXM000832 was the only sample in which compounds that could not be related to the presence of cement additives in the concrete specimens were detected.

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Appendix A

Investigation of colloid release from SiO_2 stabilised cement grout

A1 Introduction

For the waste emplaced in the silo and the waste vaults 1BTF and 2BTF, waste emplacement is followed by grouting of the waste with a cement based grout. This can be done either during operation or as a part of the sealing and closure procedures. Over the years following sealing and closure, it is expected that certain amounts of gas will be formed inside the engineered barrier as a consequence of waste form degradation. As an example, hydrogen gas is expected to be formed through the corrosion of metals under anaerobic conditions.

In order to prevent the build-up of a large gas pressure inside the engineered barriers, the gas has to be transported out of the repository. This requires both that the main engineered barriers are provided with a system for gas release but also that the cement grout is sufficiently permeable. To ensure a high permeability, the water to cement ratio of the grout needs to be sufficiently large in order to create a porous grout. However, producing grout with a high w:c ratio is not straightforward as this may cause the grout to separate into one phase rich in water and cement and one phase rich in gravel.

In order to prevent such separation, different stabilising additives can be used. Since the start of operation of the silo in SFR, cellulose derivatives have been used as stabilising agent in the cement grout used to grout the waste. However, as degradation of cellulose lead to the formation of isosaccharinic acid (Glaus and Van Loon 2008), a complexing agent, it is suggested that the cellulose derivatives should be replaced with another agent that do not form complexing degradation products.

As an alternative to cellulose derivatives, it has been suggested that colloidal silica in suspension should be used instead as a stabilising agent. However, the used of colloidal silica raises concerns that SiO_2 colloids may be released and affect the transport of the radionuclides out of the repository.

The purpose of this study is therefore to investigate colloid release from two different types of cement grout, one consisting of only cement and water and the other containing also colloidal silica as a stabilising agent.

A2 Description of the specimens

The specimens comprised one core of standard cement paste and one core made from cement containing also colloidal SiO_2. The two cores had a different appearance as shown in Figure A-1. The cement core without silica was dark grey and had a harder surface (left image) whereas the cement with the silica was light grey with a softer surface (right image).

Figure A-1. *The cement core without silica (left) and with silica (right).*

A3 Sample preparation

The samples were prepared for Photon Cross Correlation Spectroscopy (PCCS) by first crushing the cylinders with a hammer (Figure A-2). This was followed by mixing the cement with 50 ml of distilled water and left to equilibrate for two weeks (Table A-1). Following equilibration, water samples were analysed with respect to pH, colloid distribution (PCCS), zeta potential (surface potential related to surface charge) and for Si and Ca in solution by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

Just after mixing the appearance of the water containing the two types of cement differed with water containing cement with colloidal silica being somewhat cloudy whereas water containing standard cement paste was clear (Figure A-3 and A-4.)

Table A-1. The samples analysed in this study.

Sample name*	Weight (g)
U1	1.227
U2	2.126
U3	2.140
U4	2.056
U5	1.798
M1	1.385
M2	2.530
M3	1.962
M4	1.016
M5	2.267

* U denotes cement without SiO_2 and M cement with SiO_2.

Figure A-2. Samples from the cement cores. The closest specimens are made from standard cement paste while the upper specimens are made from cement blended with SiO_2.

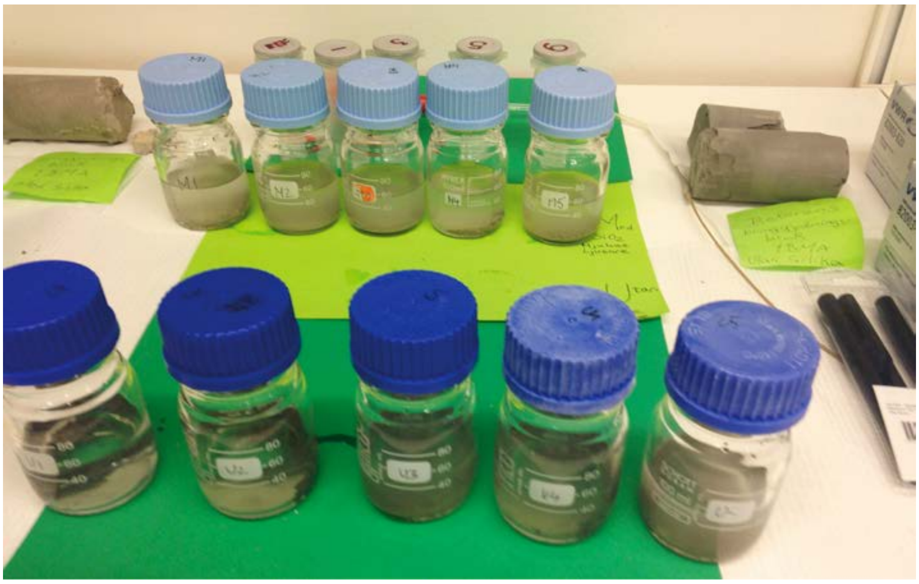

Figure A-3. Samples from the cement cores in distilled water before equilibration. The closest specimens are made from standard cement paste while the upper specimens are made from cement blended with SiO_2.

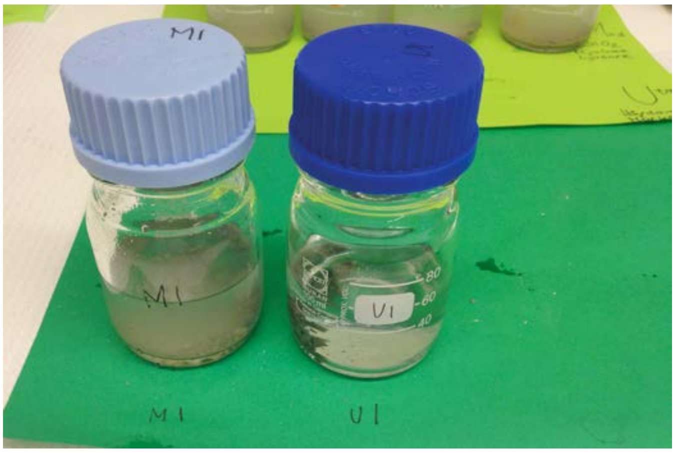

Figure A-4. Container M1 (left) contains cement with SiO_2 and U1 contains cement without SiO_2. M1 was initially cloudy and particles could be visually observed in the water phase. U1 had a very clear water phase from the start of the experiment.

A4 Results

A4.1 Mechanical properties

The cement with and without SiO_2 had different mechanical properties. The material without SiO_2 was very hard with a dark grey color and difficult to crush with a hammer. The cement containing colloidal silica was light grey and soft with a talc-like feeling and could easily be crushed with a hammer.

A4.2 Chemical and physical properties

The visual appearance of the water in contact with the two types of grinded cement was initially very different. From start the solution in contact with cement containing SiO_2 was cloudy and particles could be visually observed in the solution. The solutions in contact with cement without SiO_2 were clear and transparent. After 2 weeks equilibration, cloudiness could be detected just above the cement bed for cement containing SiO_2 whereas the remaining water was clear. Sampling was made at a distance of about 1 cm from the surface of the water to avoid sampling of cloudy water. However, in the containers with cement containing SiO_2 samples were also taken in the cloudy part just above the cement bed.

The temperature during the measurement was kept constant at 20 °C. A PCCS signal below 10 kcps corresponds roughly to that of ordinary tap water. A positive zeta-potential corresponds to a positive surface charge. A summary of the results is presented in Table A-2.

Table A-2. Summary of the results from the different analyses.

Sample name*	pH in solution	PCCS signal (kcps) 1.	PCCS signal (kcps) 2.	Colloids in solution	Zeta-potential (mV)	ICP-OES [Si] (ppm)	ICP-OES [Ca] (ppm)
M1 (1 cm down)	> 12	1		No			
M2 (1 cm down)	> 12	5		No			
M3 (1 cm down)	> 12	76		Yes			
M4 (1 cm down)	> 12	108		Yes			
M5 (1 cm down)	> 12	-	-	-			
M1 (above bed)	> 12	40	30	Yes	+34	1.9	387
M2 (above bed)	> 12				+22	0.4	431
M3 (above bed)	> 12	158	68	Yes	+5	1.0	430
M4 (above bed)	> 12				+38	1.0	185
M5 (above bed)	> 12	150		Yes	+21	1.8	461
U1 (above bed)	> 12	1		No	-	0.4	417
U2 (1 cm down)	> 12	1		No	-	0.3	433
U3 (1 cm down)	> 12	1		No	-	0.3	418
U4 (1 cm down)	> 12	1		No	-	0.3	423
U5 (1 cm down)	> 12	2		No	-	0.3	428

* M: With SiO_2, U: Without SiO_2.

The results from the PCCS analyses show that the amount of colloids in the solutions containing cement without silica is below the detection limit of the method.

For cement containing silica the solution about 1 cm above the bed of the cement was still cloudy at the time of analysis whereas further up the water was completely transparent. In two of the samples (M3 and M4) PCCS analysis confirmed the presence of particles in solution with the dominating particles in the upper nano range, i.e. a few hundred to a thousand nanometers. Analysis of M1 and M3 just above the bed confirmed the presence of particles in solution.

The particles in M1–M5 (above bed) also gave positive zeta-potentials, interpreted as positive net surface charge. This indicates that the particles found are not just SiO_2 but that a specie with a positive charge is bound to the surface. In this system Ca^{2+} which prevails in large amounts in the solutions can bind to the SiO_2 surface and give a net positive charge. The ICP-OES analysis of Ca and Si in the system shows that Ca is homogenously distributed in the water columns in the flasks. Si is though more concentrated to the cloudy part just above the cement bed in the M samples. This confirms the existence of colloids in the solution.

A5 Summary and conclusions

In this Appendix the results from an investigation of the properties of two types of cement grout – one containing colloidal silica as stabilising agent and one without silica – have been reported. The main focus in this study has been on colloid release from crushed cement in solution but also other properties have been investigated.

The cement core without SiO_2 was found to be hard and resistant and did not release any detectable amount of particles to the solution within the experimental time. The cement core with SiO_2 was most likely a mix of two phases of which one was cement rich and the other mainly consisted of unreacted SiO_2. SiO_2 particles seem to be released to the solution initially, but particles aggregate and sediment with time, so at equilibrium a fewer number of colloids was found in solution.

In a stagnant system such as in these experiments a pseudo equilibrium concentration will be built up above the cement bed. However, a homogenous concentration will not form in the entire water column due to aggregation and sedimentation of particles. In a system with a water flow, particles will continuously be transported away from the cement, and colloids will be released driven to reach equilibrium.

Appendix B

NMR study of degradation of organic material

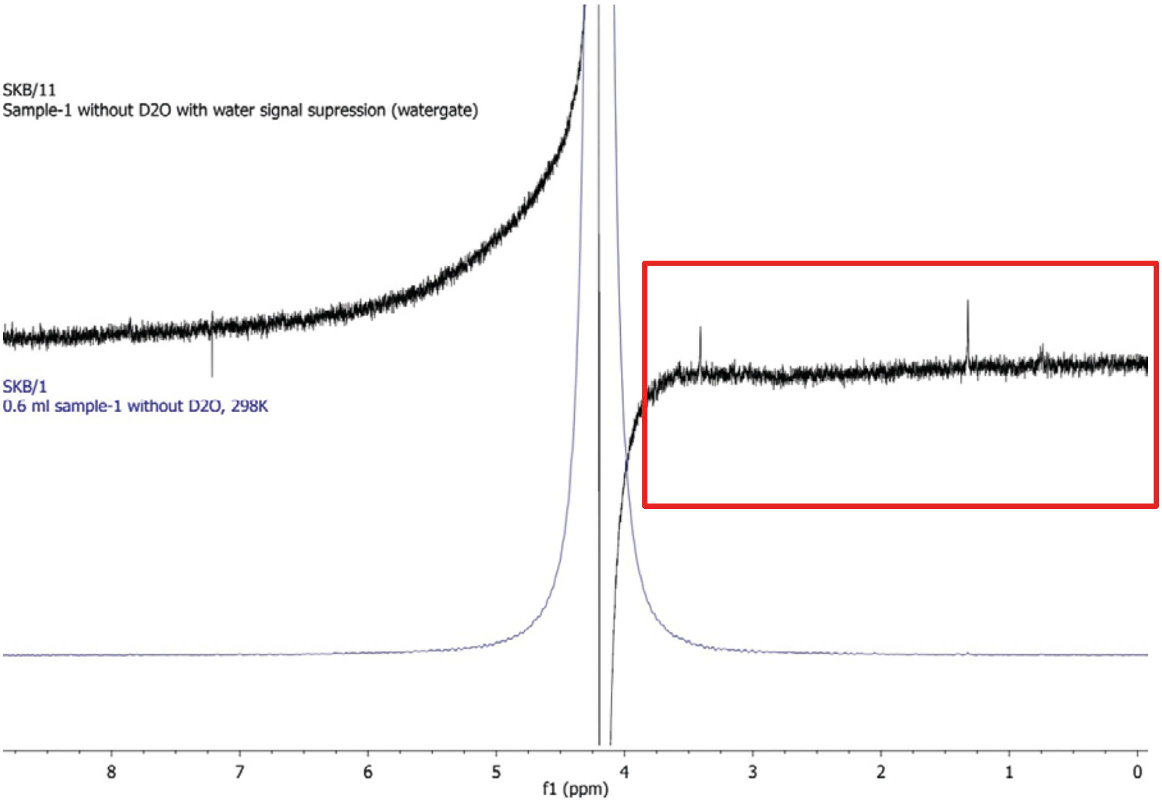

Figure B-1. *^{1}H NMR spectra of the sample taken from container # 1 with (top) and without (bottom) suppression of the water signal.*

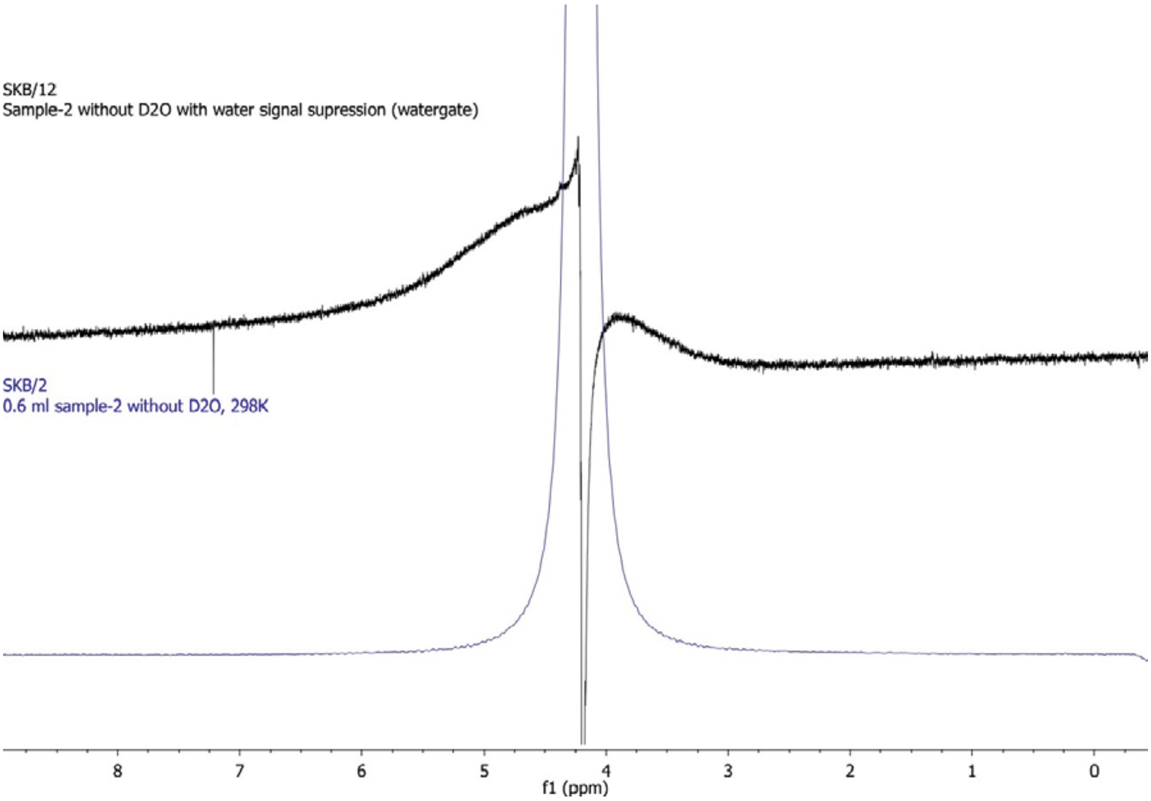

Figure B-2. *^{1}H NMR spectra of the sample taken from container # 2 with (top) and without (bottom) suppression of the water signal.*

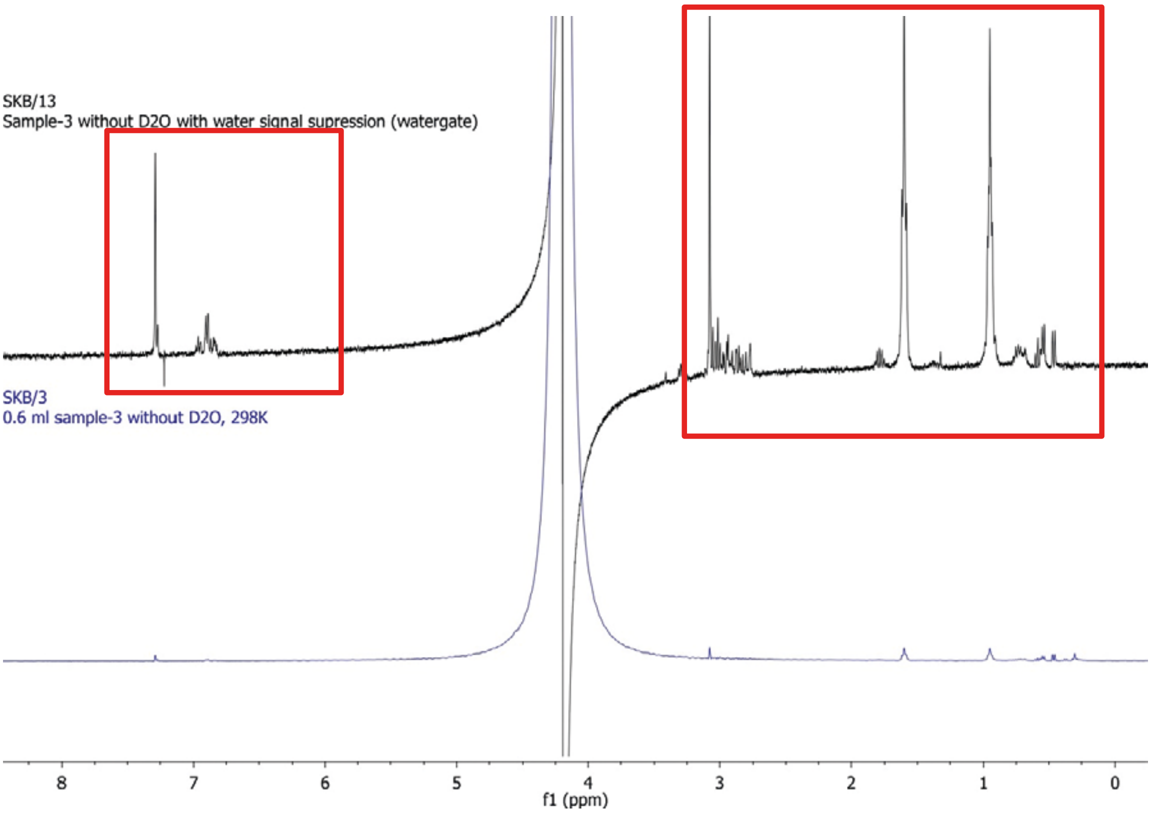

Figure B-3. *^{1}H NMR spectra of the sample taken from container # 3 with (top) and without (bottom) suppression of the water signal.*

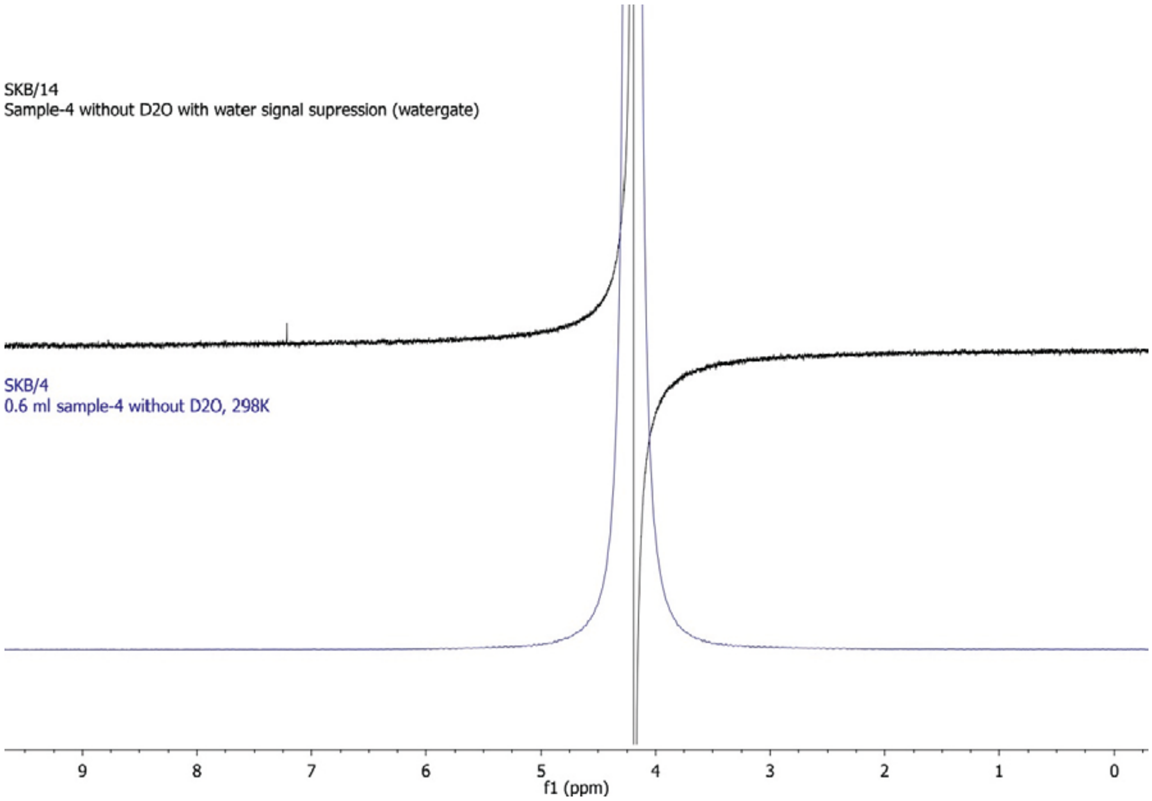

Figure B-4. *^{1}H NMR spectra of the sample taken from container # 4 with (top) and without (bottom) suppression of the water signal.*

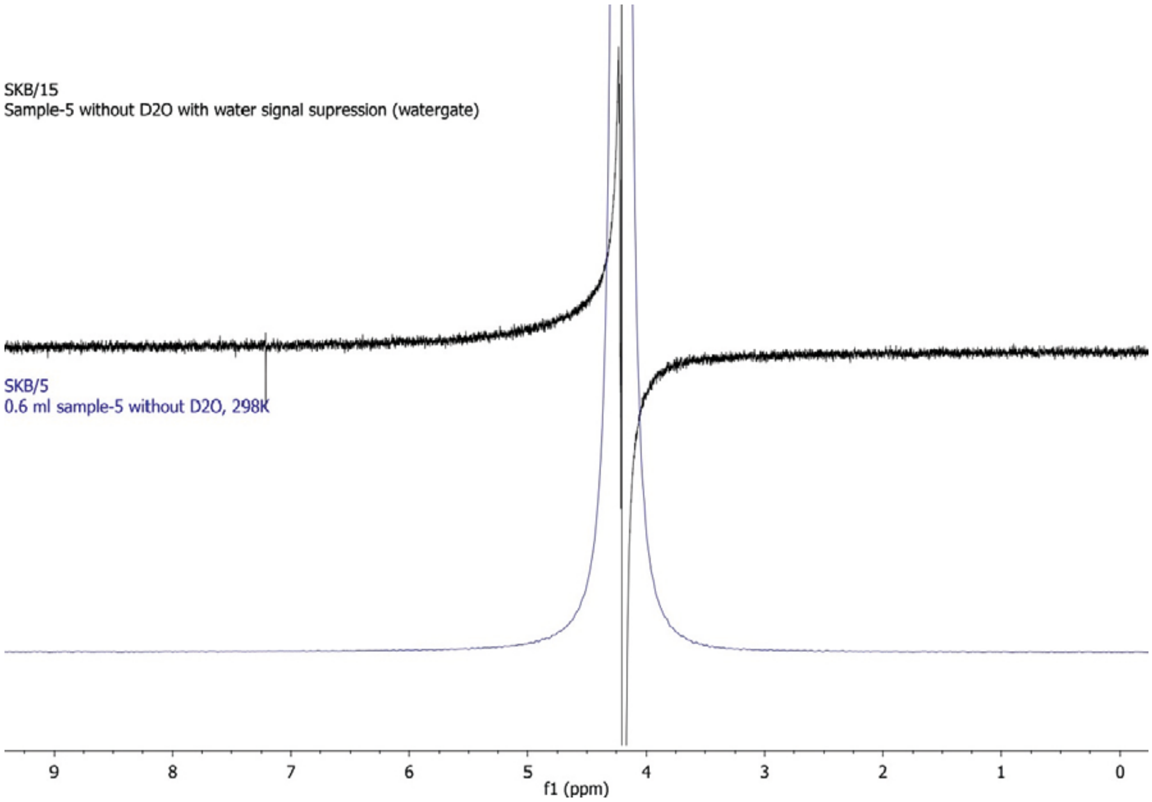

Figure B-5. *^{1}H NMR spectra of the sample taken from container # 5 with (top) and without (bottom) suppression of the water signal.*

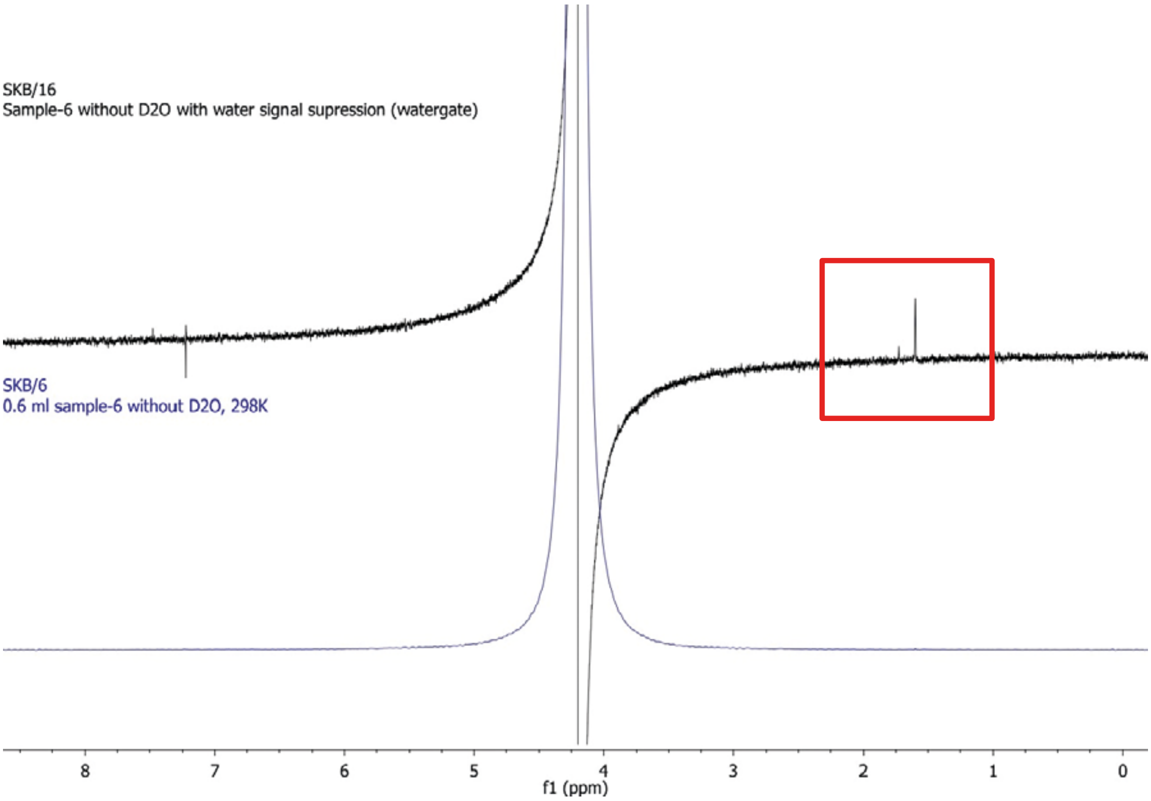

Figure B-6. ^{1}H NMR spectra of the sample taken from container # 6 with (top) and without (bottom) suppression of the water signal.

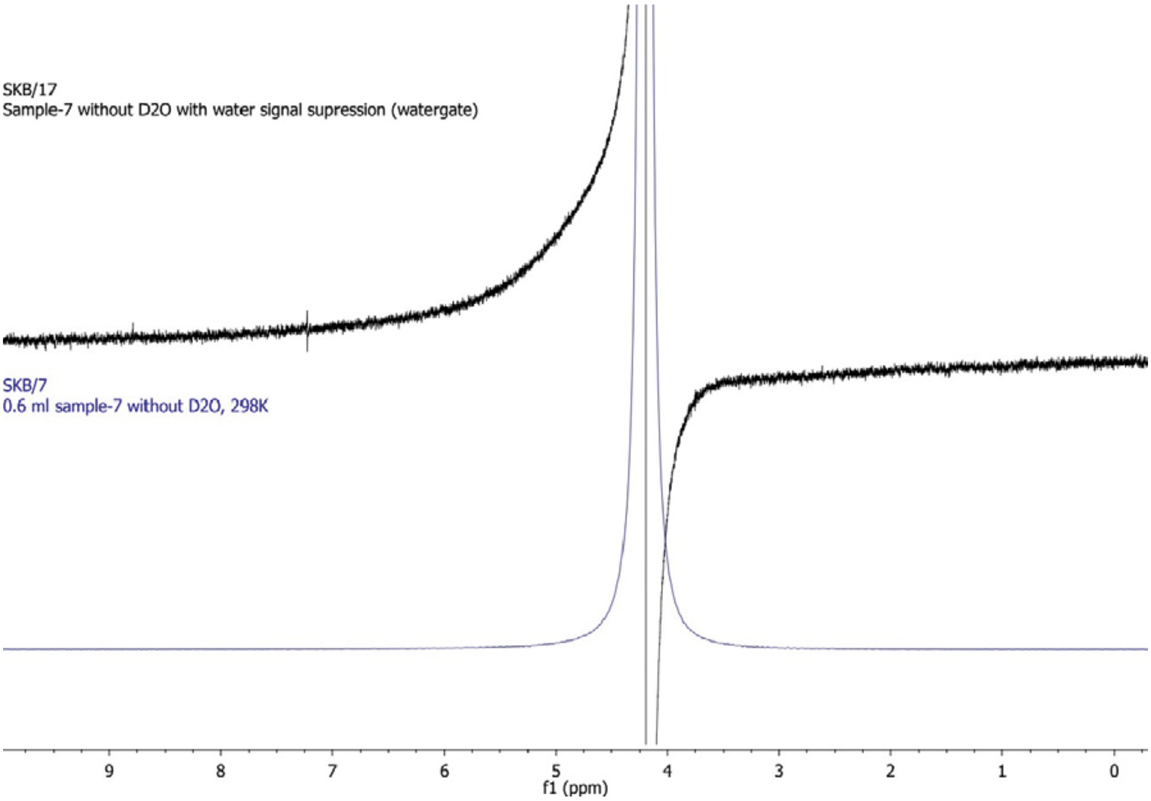

Figure B-7. ^{1}H NMR spectra of the sample taken from container # 7 with (top) and without (bottom) suppression of the water signal.

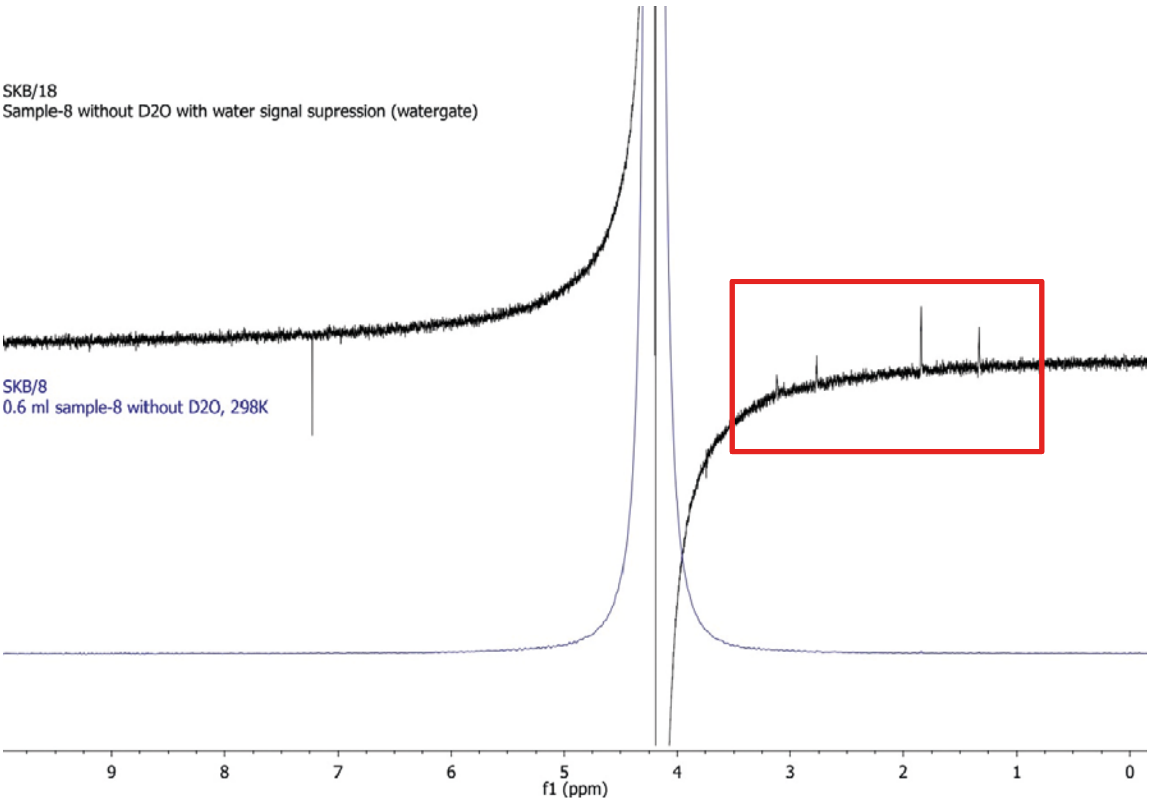

Figure B-8. *^{1}H NMR spectra of the sample taken from container # 8 with (top) and without (bottom) suppression of the water signal.*

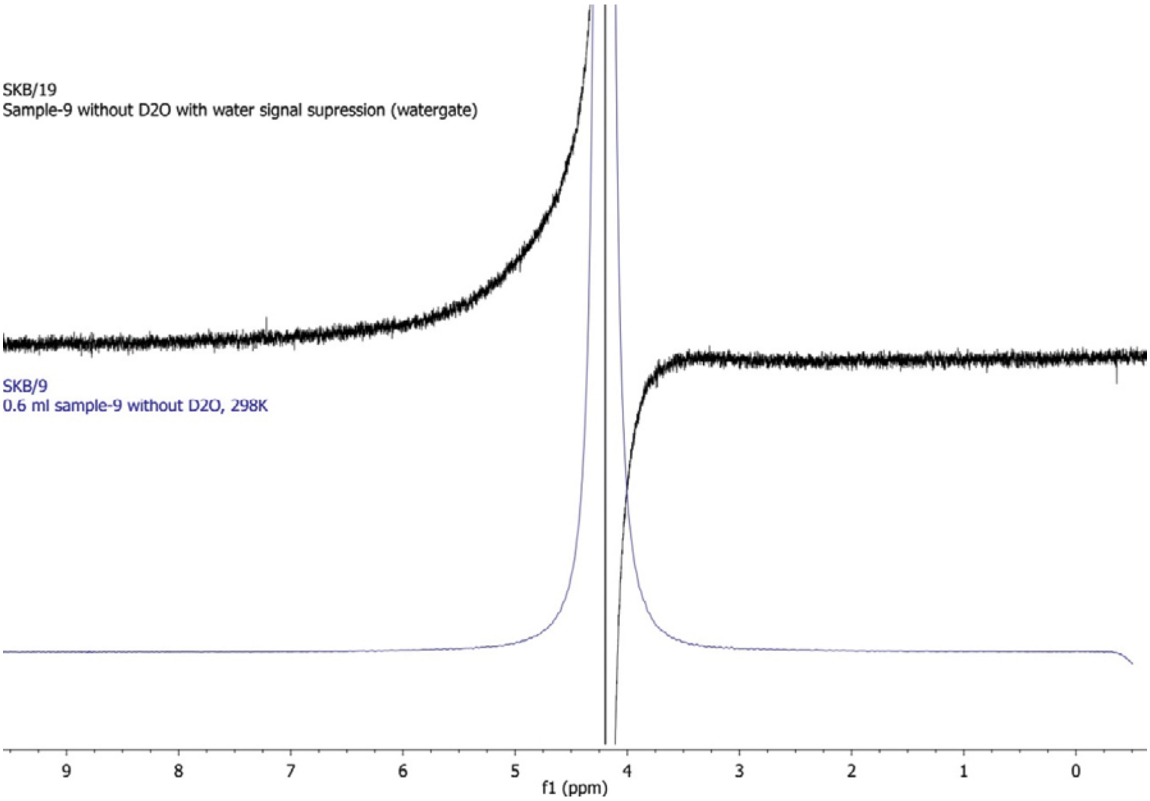

Figure B-9. *^{1}H NMR spectra of the sample taken from container # 9 with (top) and without (bottom) suppression of the water signal.*

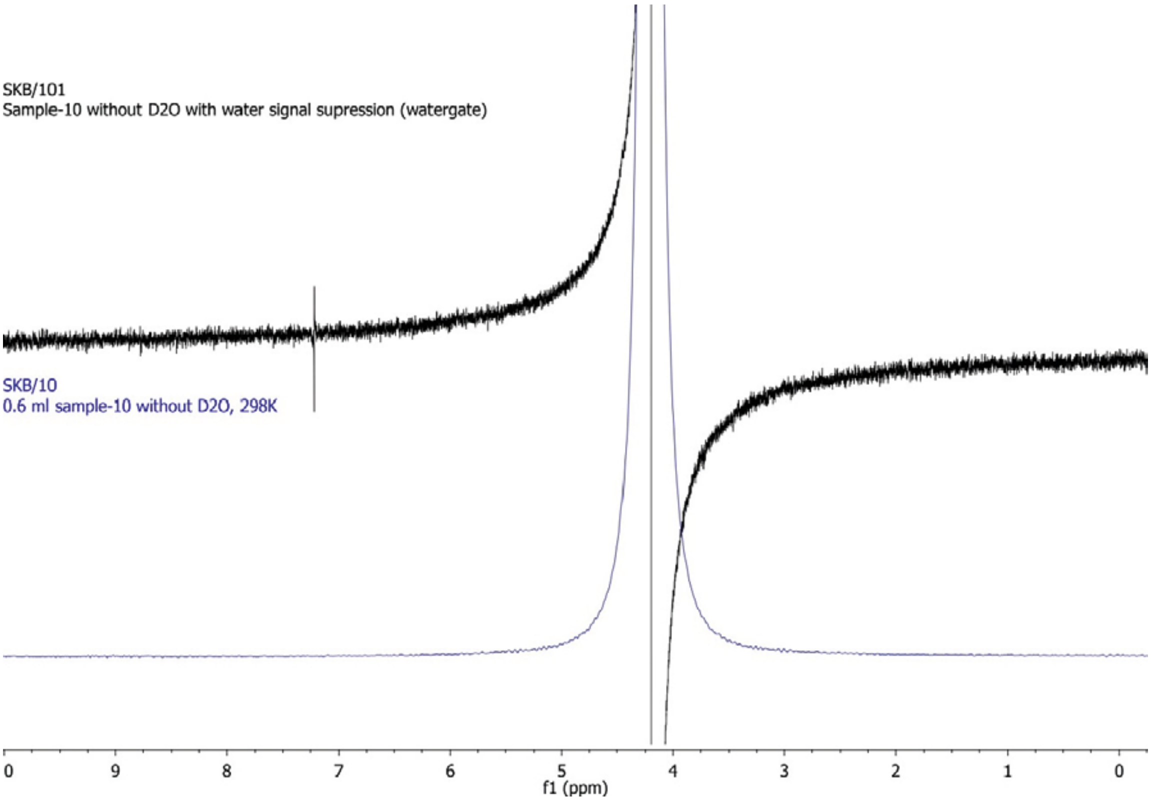

Figure B-10. *^{1}H NMR spectra of the sample taken from container # 10 with (top) and without (bottom) suppression of the water signal.*

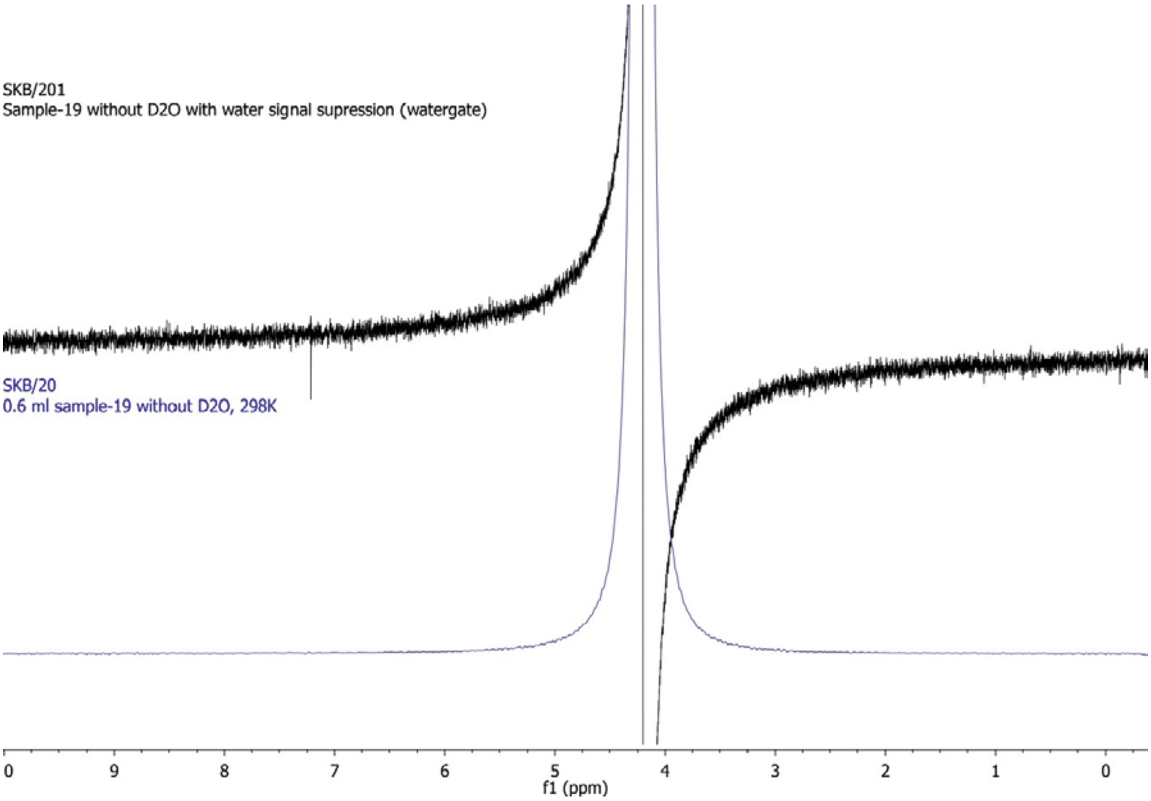

Figure B-11. *^{1}H NMR spectra of the sample taken from container # 19 with (top) and without (bottom) suppression of the water signal.*

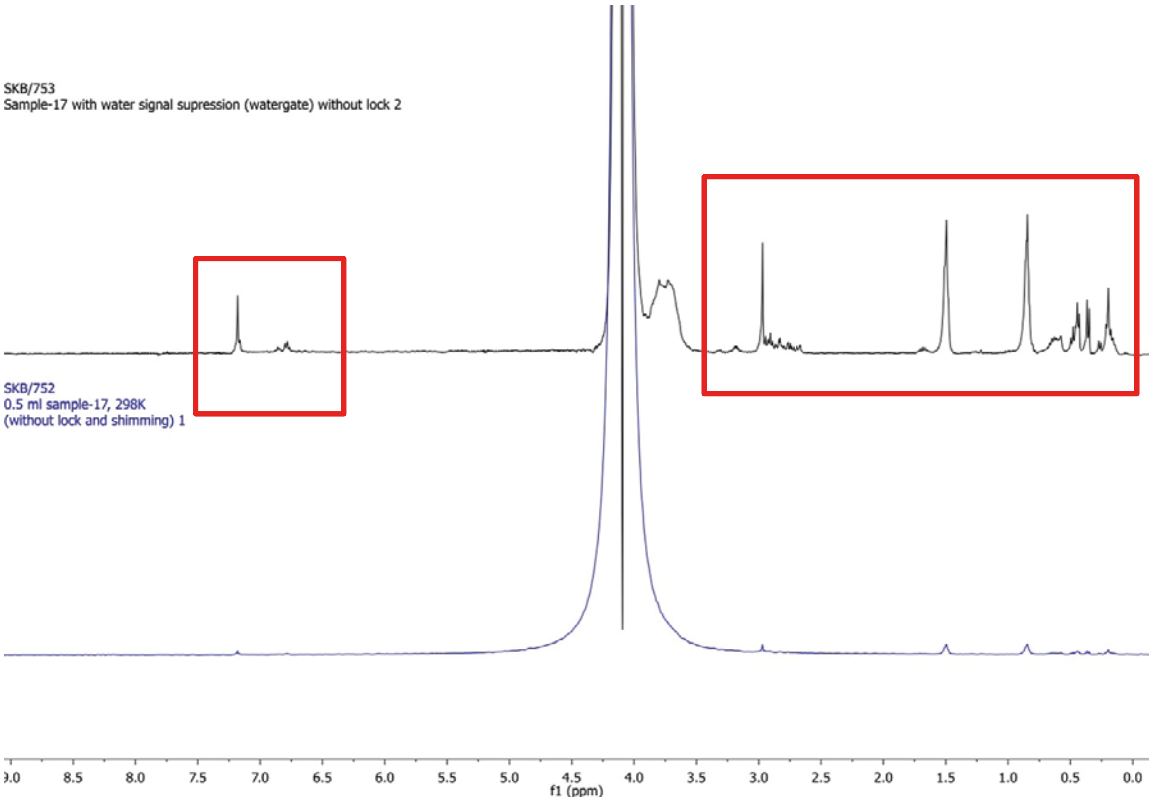

Figure B-12. *^{1}H NMR spectra of the sample taken from container # 17 with (top) and without (bottom) suppression of the water signal.*

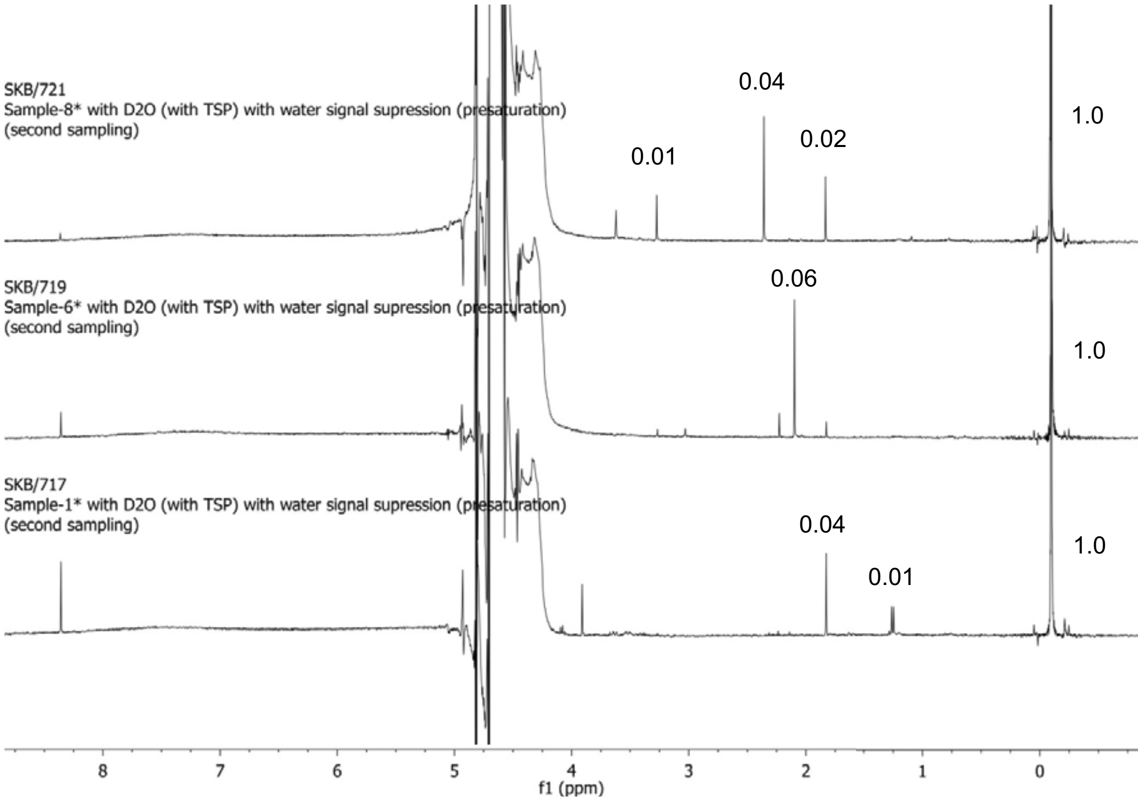

Figure B-13. *Comparison of the water signal suppressed ^{1}H-NMR spectra of the samples taken from containers # 1, 6 and 8 (containing 10 % D_2O and the reference, TSP-d_4 in 3.5 mM concentration in each samples). The numbers are indicating the relative signal intensities.*

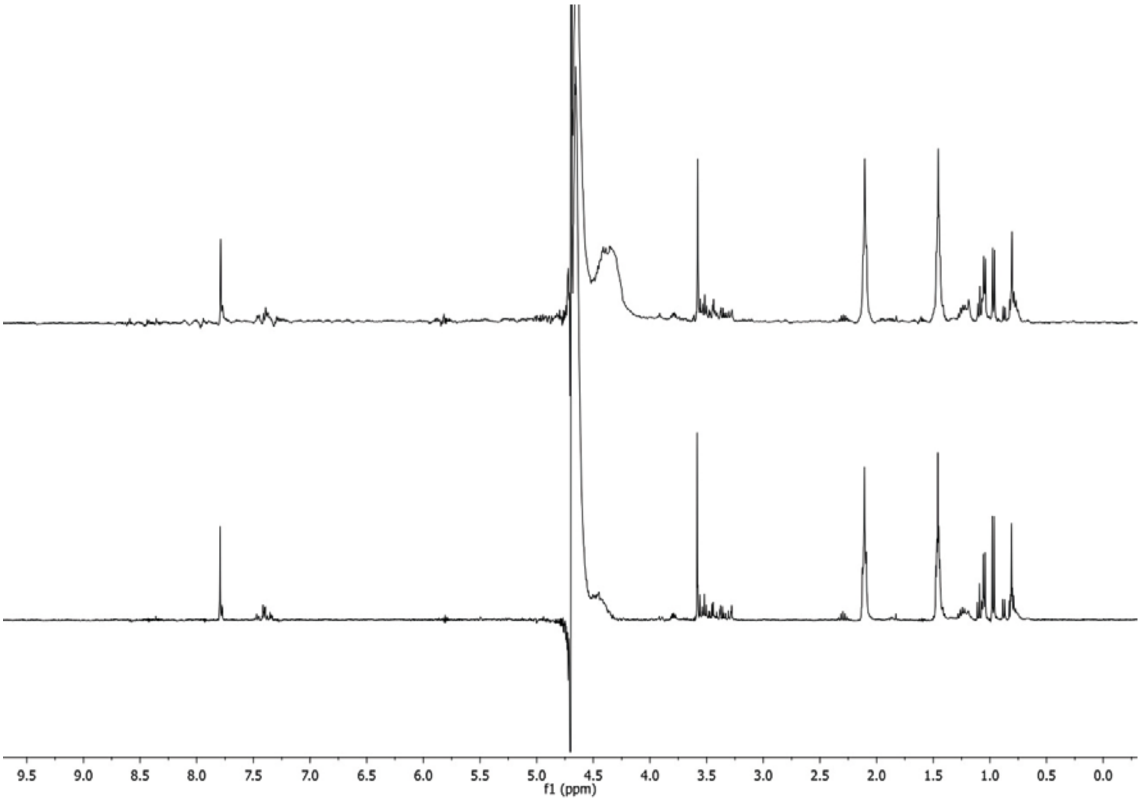

Figure B-14. *Comparison of the water signal suppressed ^1H NMR spectra of the samples taken from container # 3 (bottom) and container # 17 (top) (containing 10 % D_2O).*

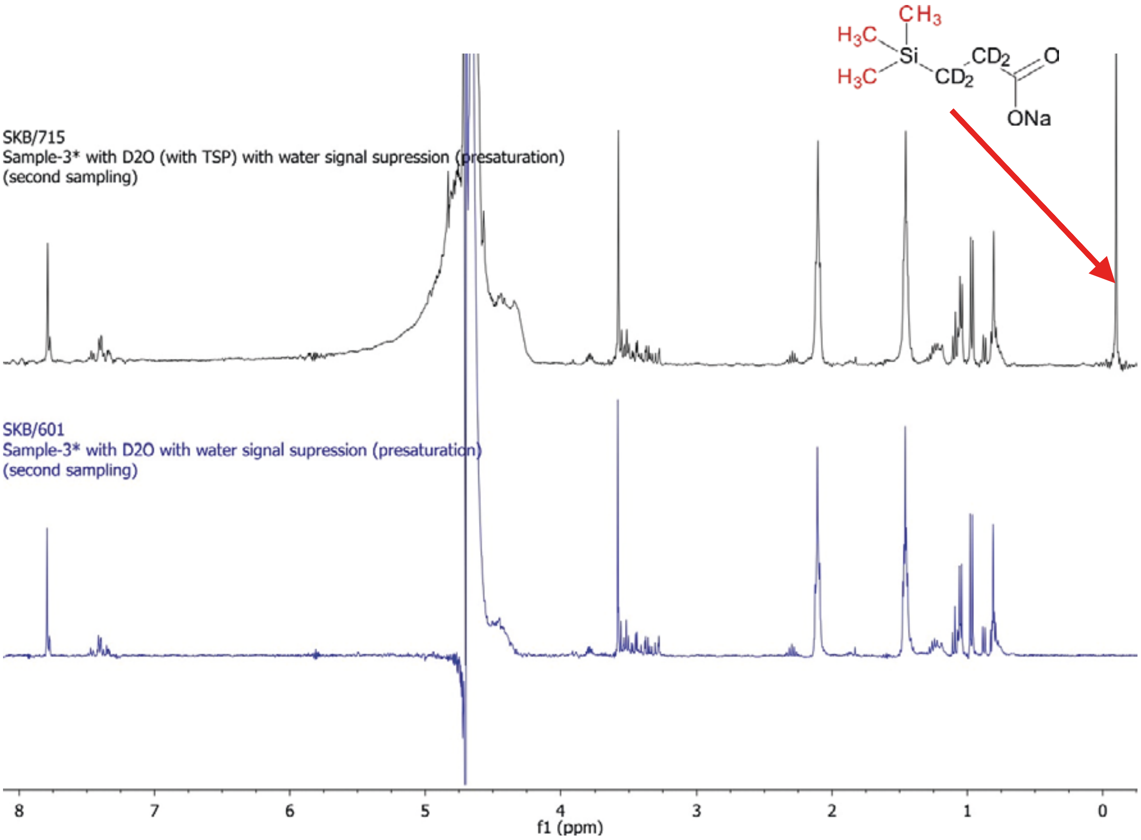

Figure B-15. *Water signal suppressed ^1H NMR spectra of the sample taken from container # 3 containing 10 % D_2O without (bottom) and by added (top) reference compound (TSP-d_4).*

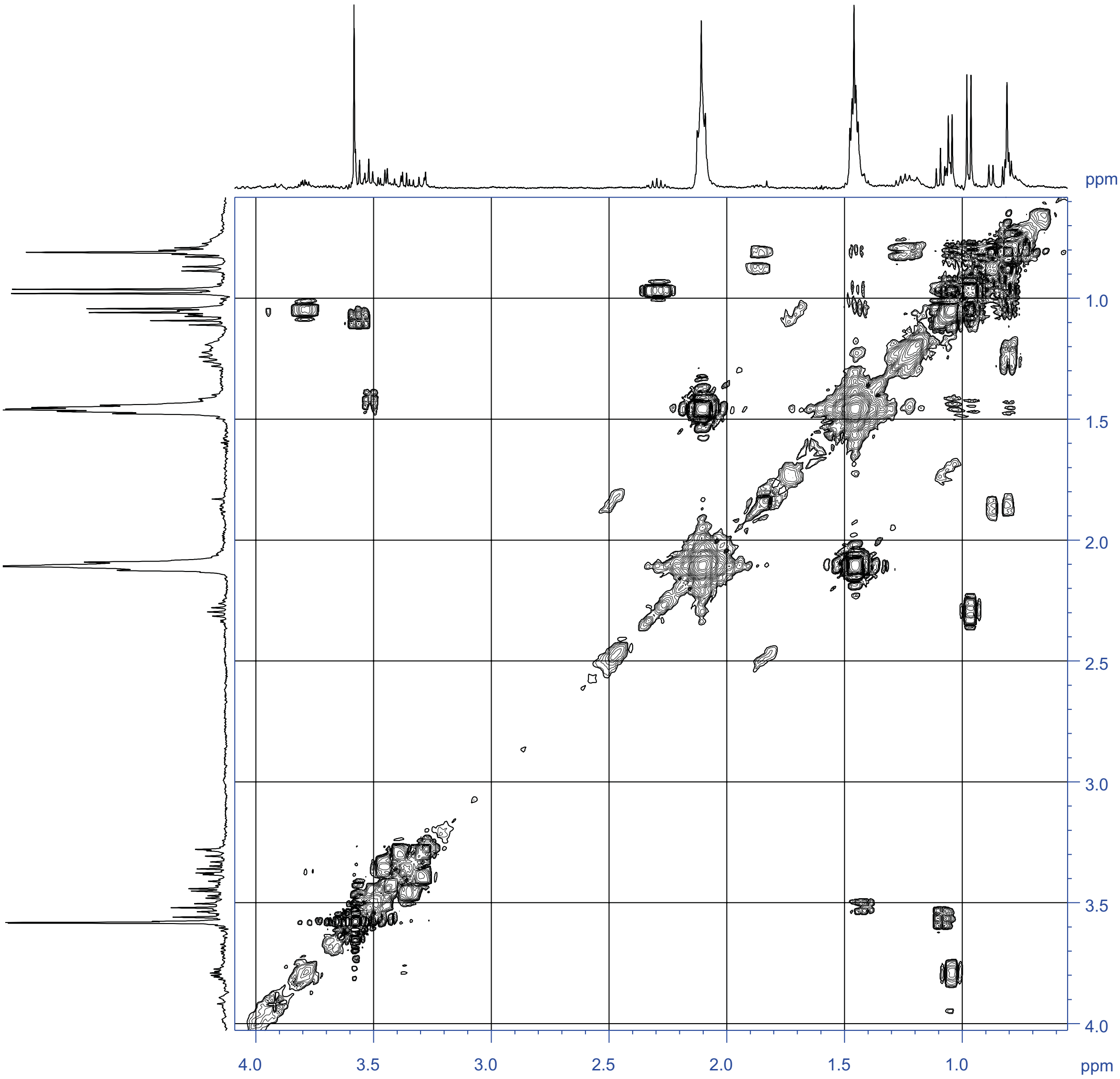

Figure B-16. *^1H-^1H-COSY NMR spectrum of sample taken from container # 3 containing 10 % D_2O. The spectrum was measured using a pulse sequence with water pre-saturation.*

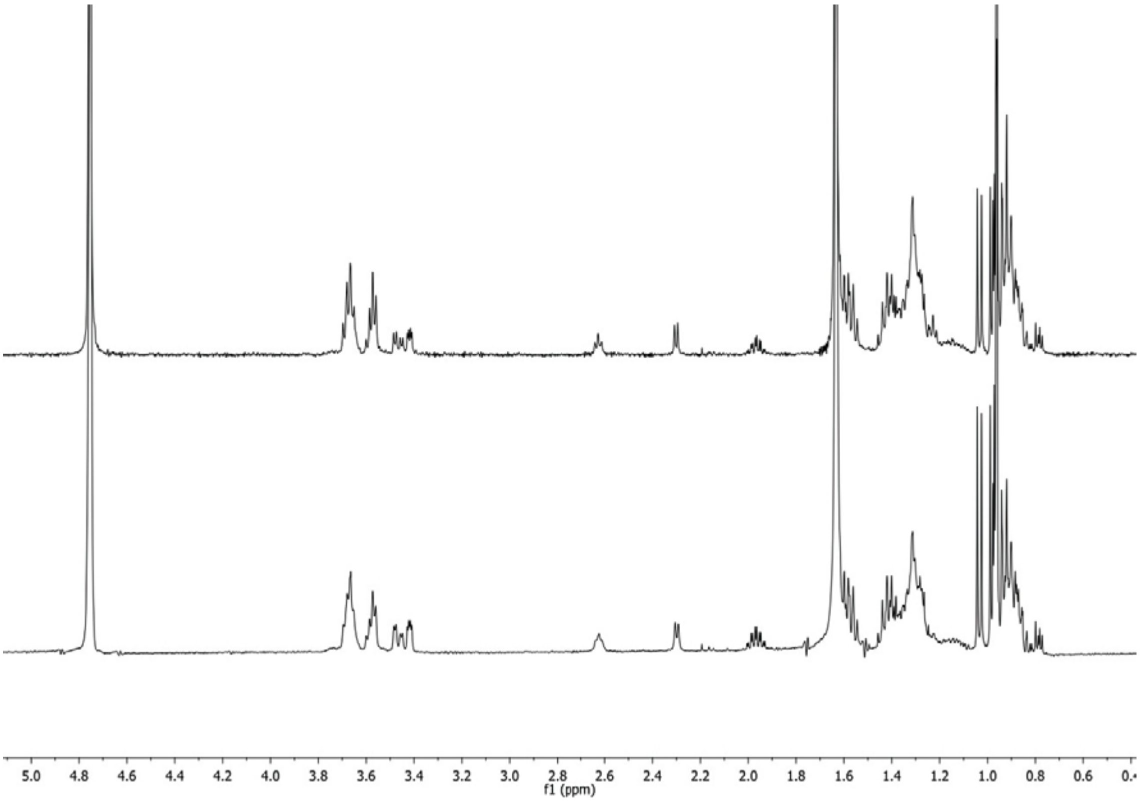

Figure B-17. *^{1}H NMR spectra measured in the $CDCl_3$ phase from the extraction experiments using samples from container # 3 (bottom) and container # 17 (top).*

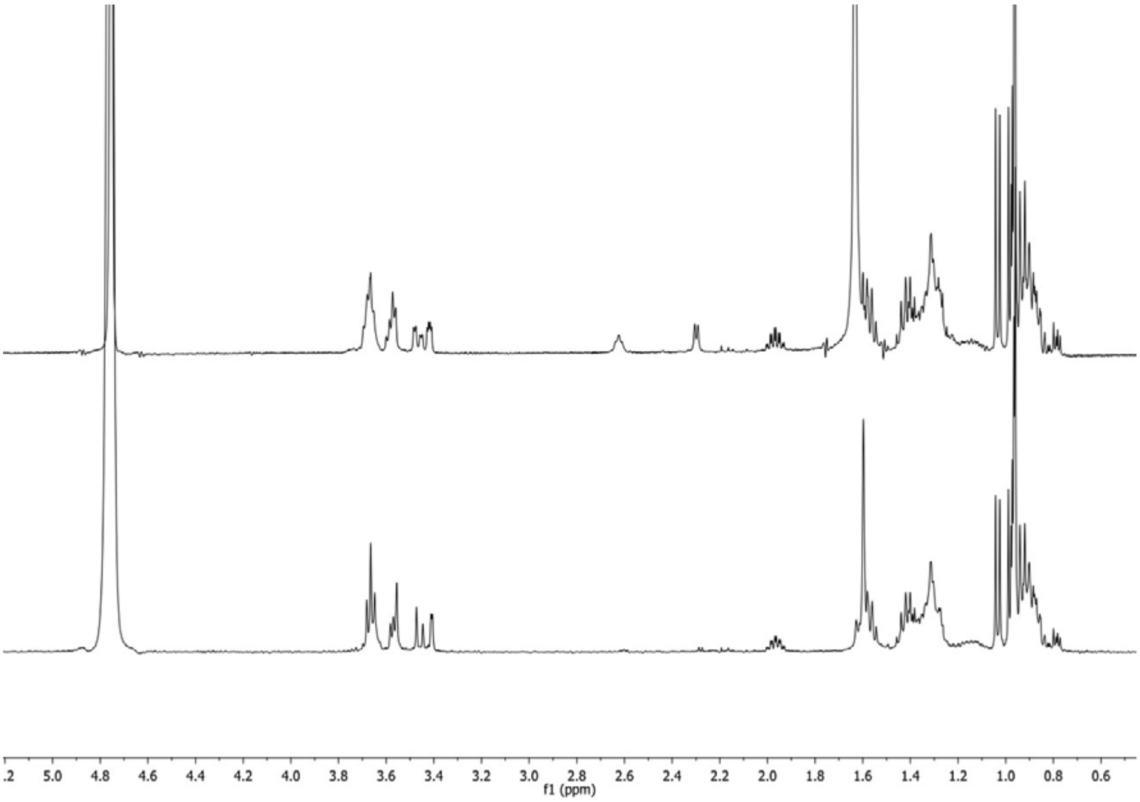

Figure B-18. *^{1}H NMR spectra of the organic phase extracted with $CDCl_3$ from the sample taken from container # 3 (top). The spectrum recorded after addition of a few drops of D_2O (bottom).*

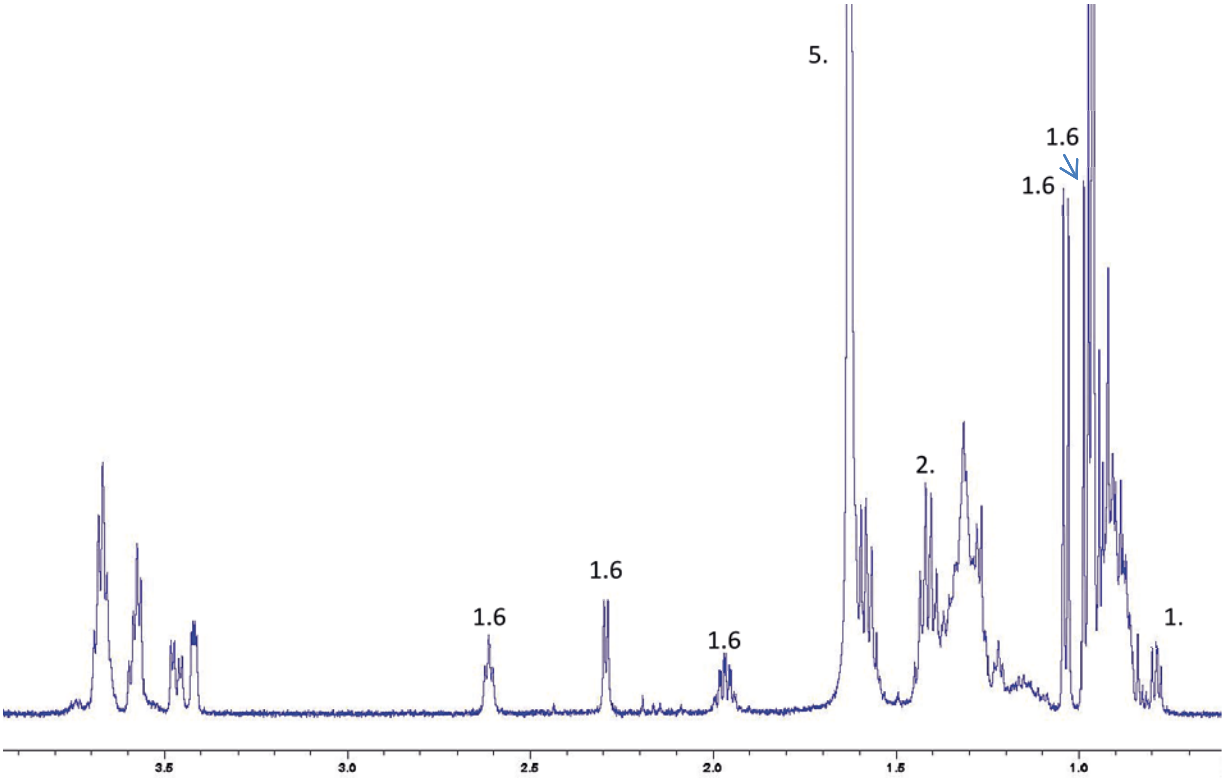

Figure B-19. *500 MHz ^1H NMR spectrum of the $CDCl_3$ phase extracted from a sample from container # 3 showing the diffusion coefficients for some of the signals (in the units of 10^{-9} m^2/s).*

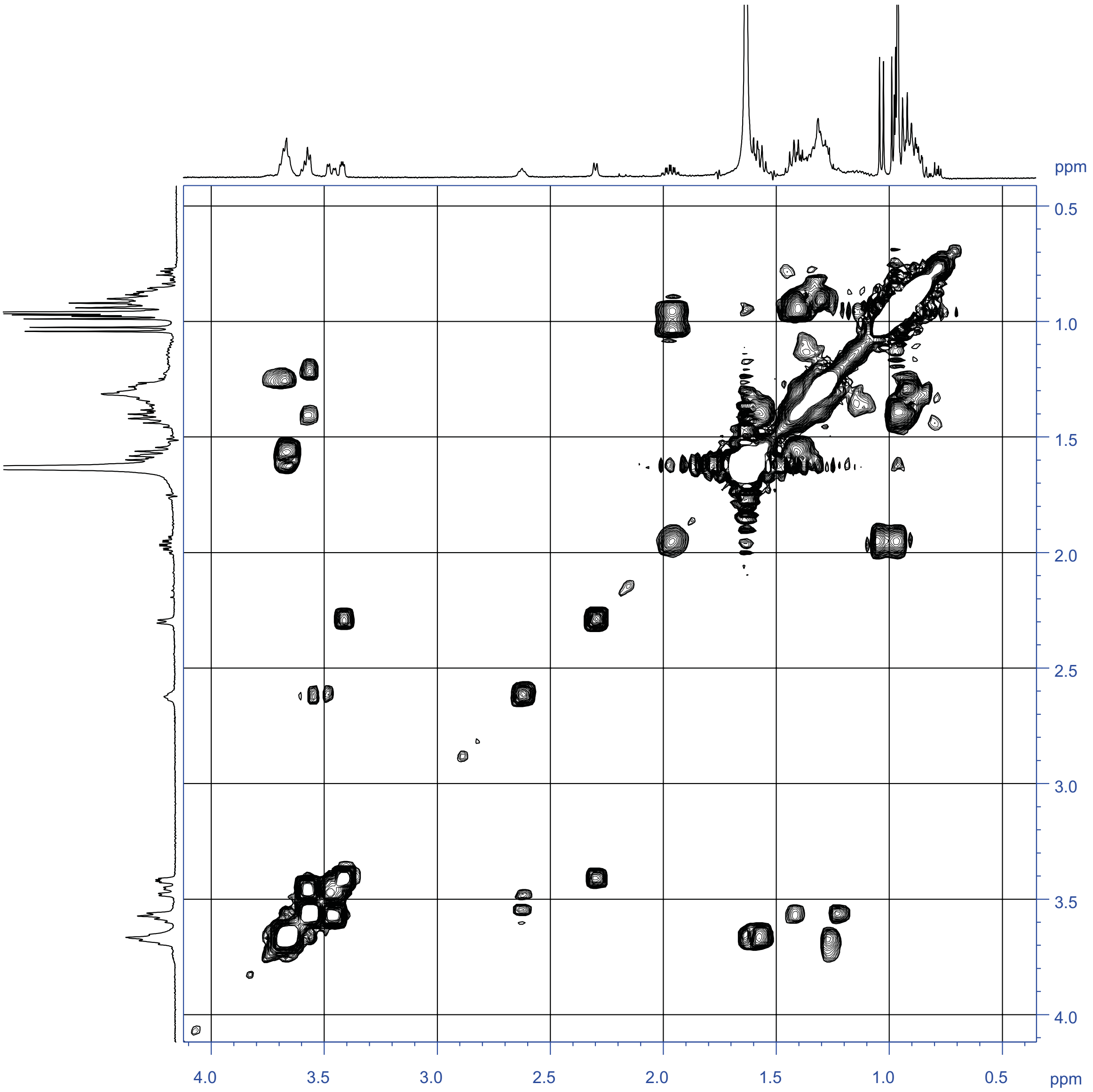

Figure B-20. *${}^{1}H$-${}^{1}H$- COSY NMR spectrum of the $CDCl_3$ phase extracted from a sample from container #3.*

Appendix C

Study of specimens from field scale concrete experiments

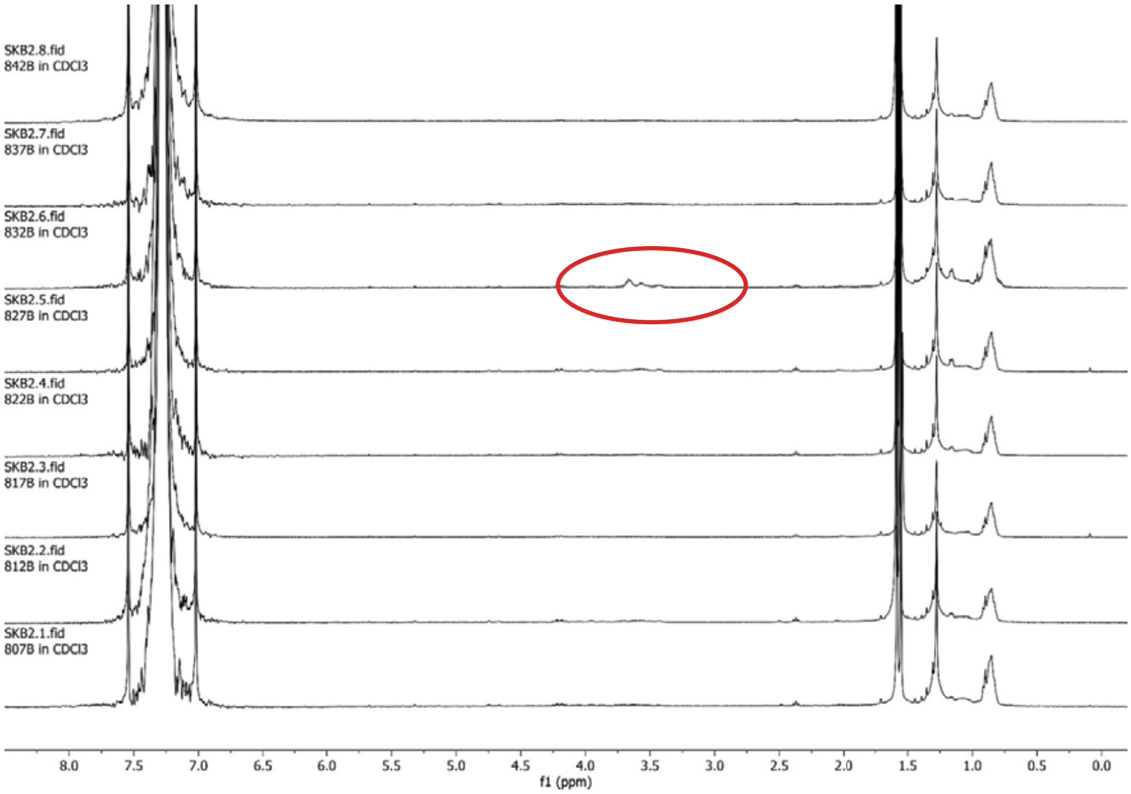

Figure C-1. *Stacked plot of the* ^{1}*H-NMR spectra measured in* $CDCl_3$.

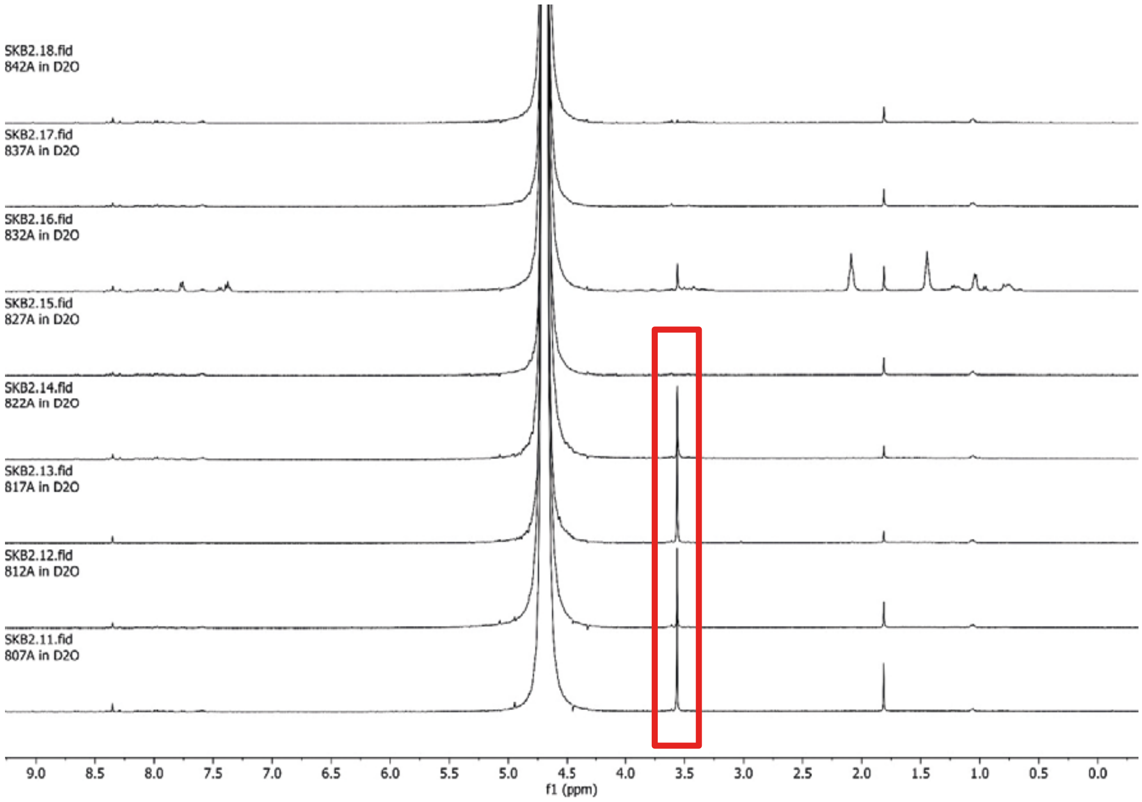

Figure C-2. *Stacked plot of the ^{1}H-NMR spectra measured in D_2O. The signals of ethylene glycol in samples from cylinder I-2B are marked by the red rectangle.*

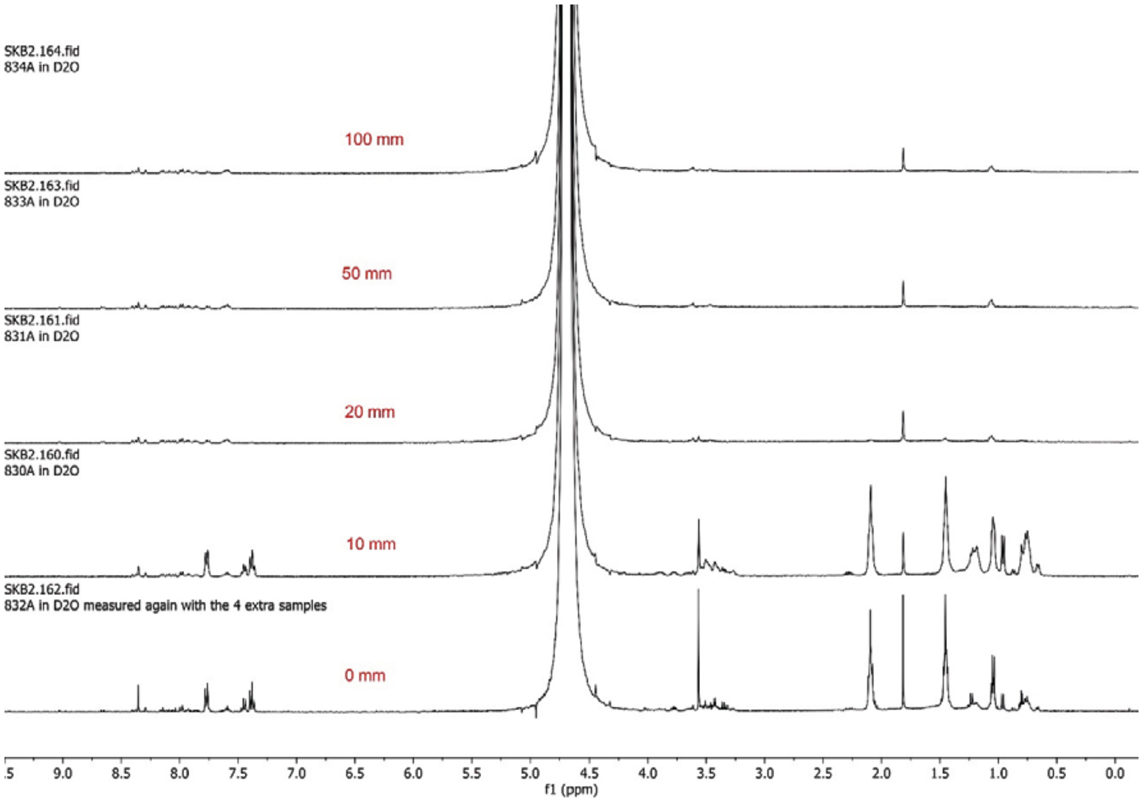

Figure C-3. *Distance dependent ^{1}H-NMR spectra of the specimens from the cement core containing rubber gloves. (The spectra were measured in D_2O by collecting 32 scans.)*

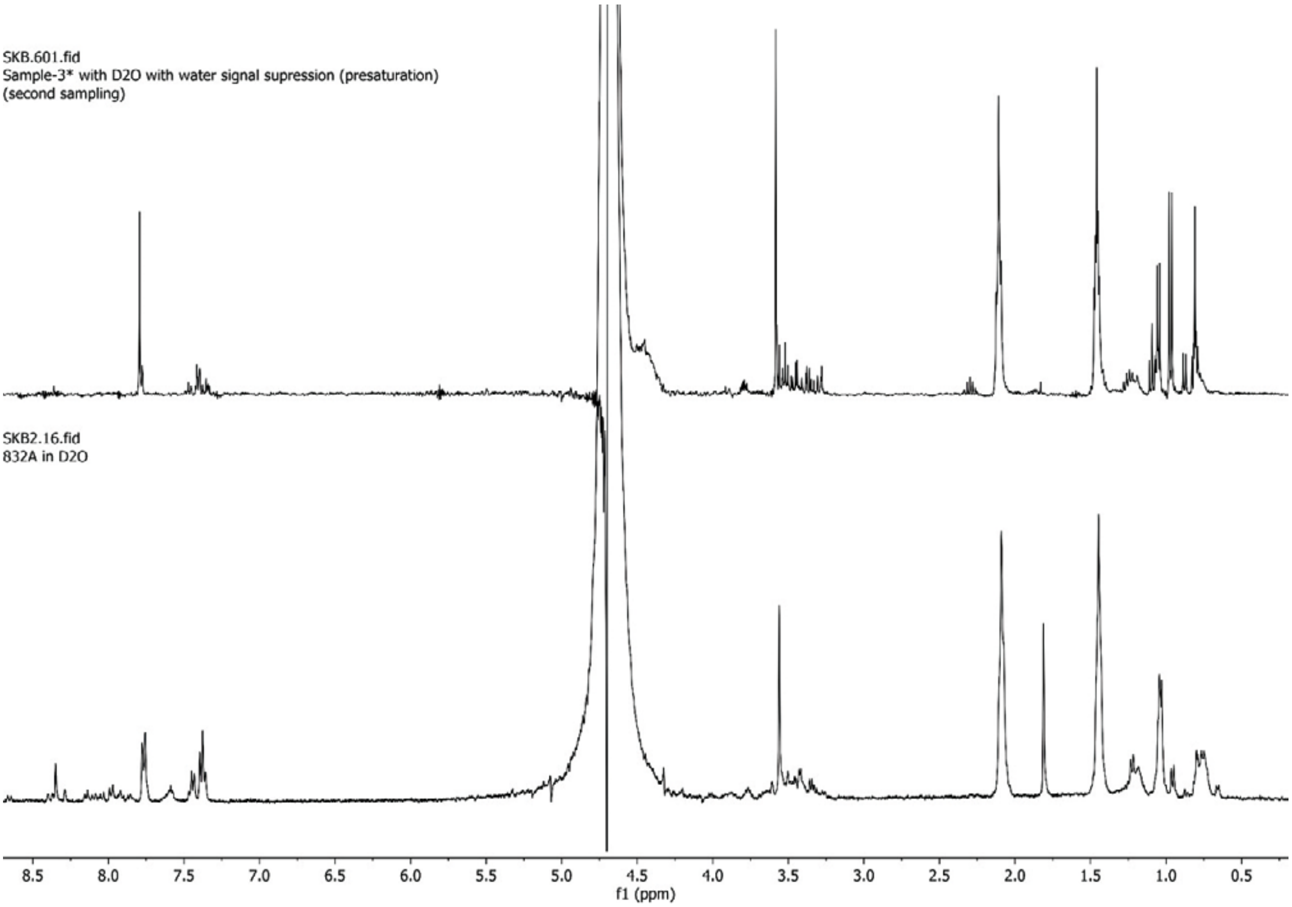

Figure C-4. *Comparison of the ^{1}H-NMR spectra of specimen FXM000832 (bottom) and the sample (top) from the cement core (Figure B-15) containing rubber gloves.*

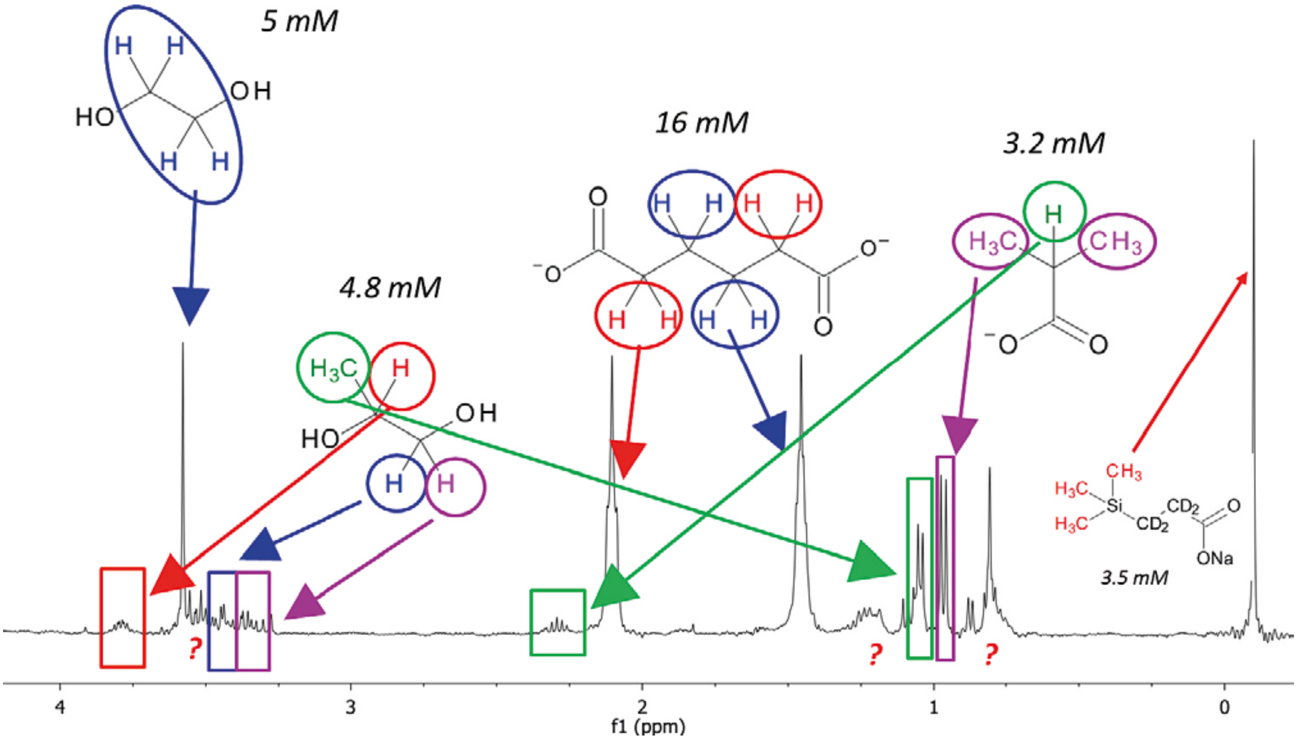

Figure C-5. *Assignments of the aliphatic ^{1}H-NMR signals of the degradation products in the cement core containing rubber gloves (spectrum and the concentrations indicated are from Figure 4-2 in the main part of this report).*

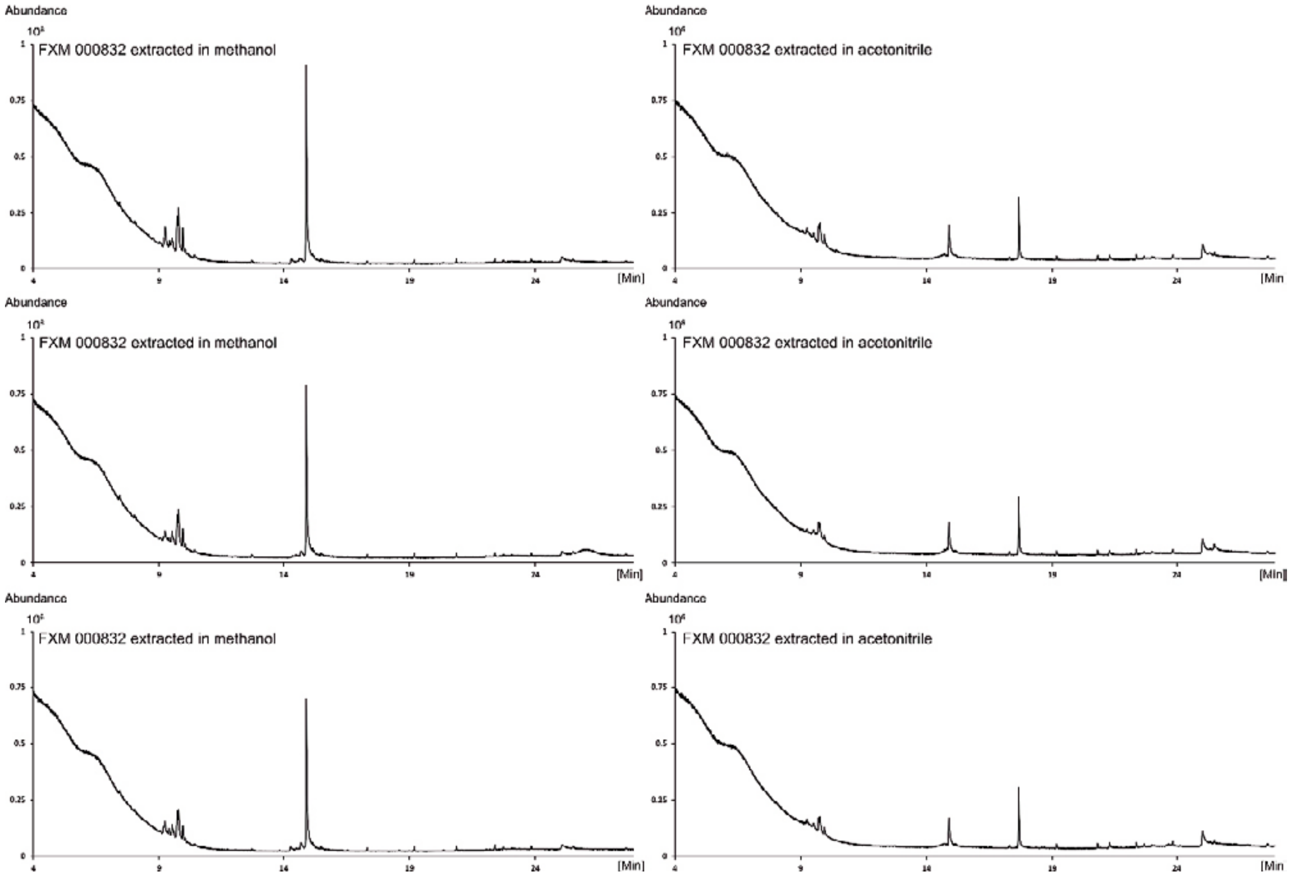

Figure C-6. *Chromatograms obtained from samples extracted with ultrasound (UAE) using MeOH (left), and MeCN (right). Liquid injection. Three different injections per sample.*

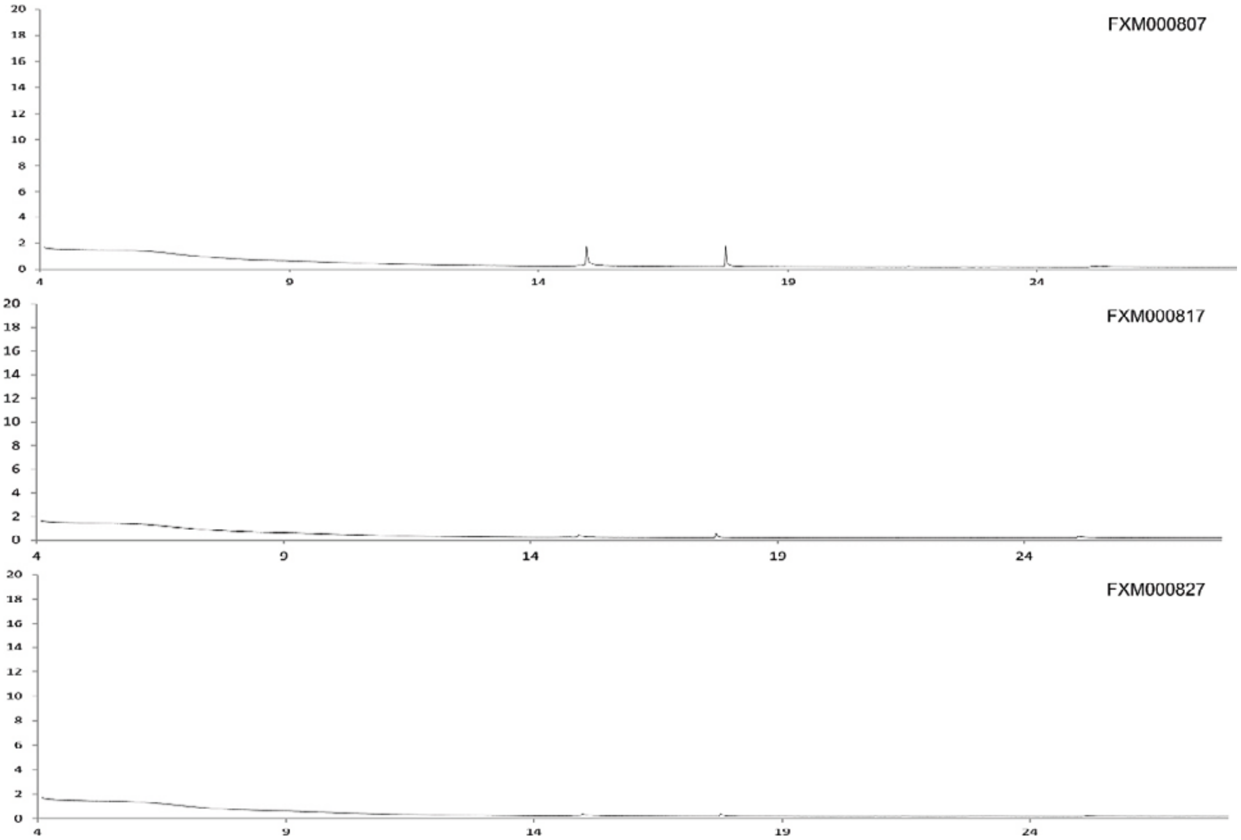

Figure C-7. *Representative examples of chromatograms obtained from samples extracted with ultrasound (UAE) using MeCN. Liquid injection.*

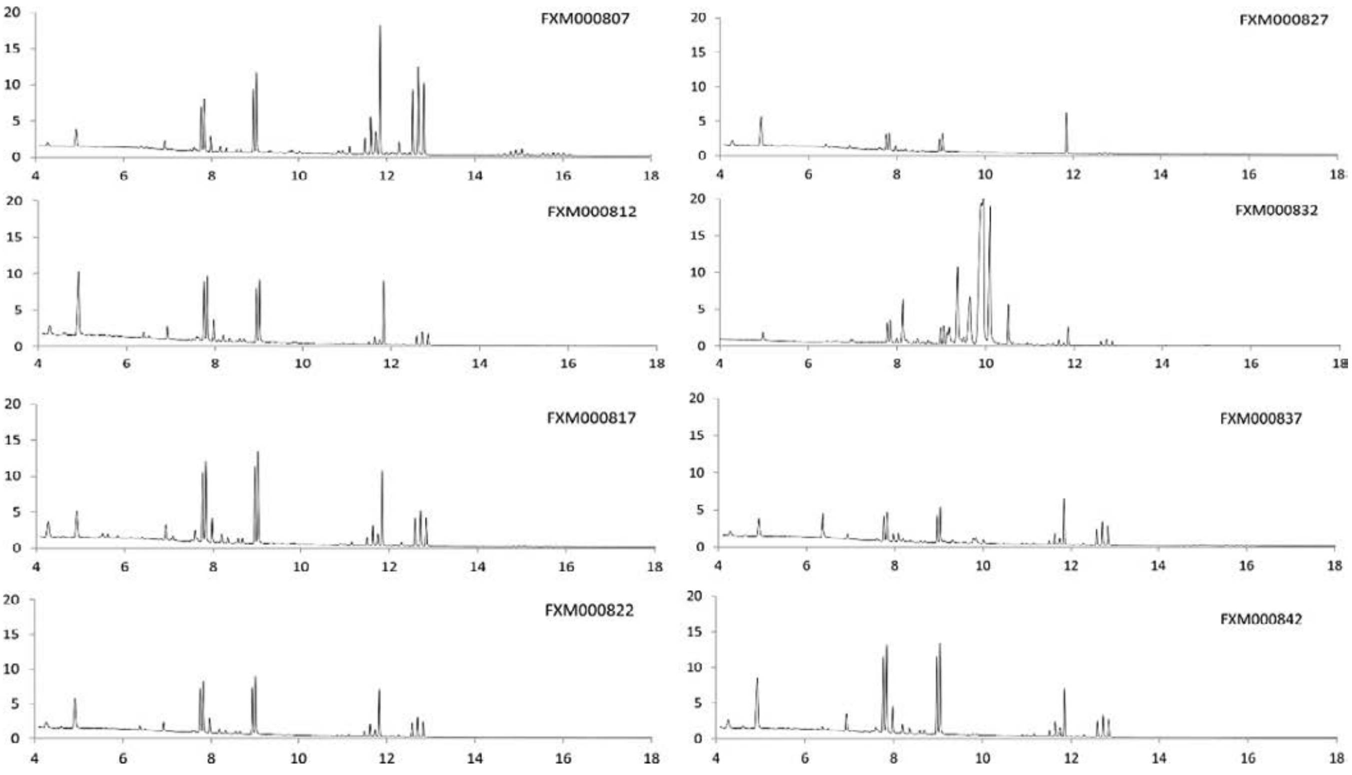

Figure C-8. *Chromatograms obtained from samples extracted with ultrasound (UAE) using water, and treated with SPME.*

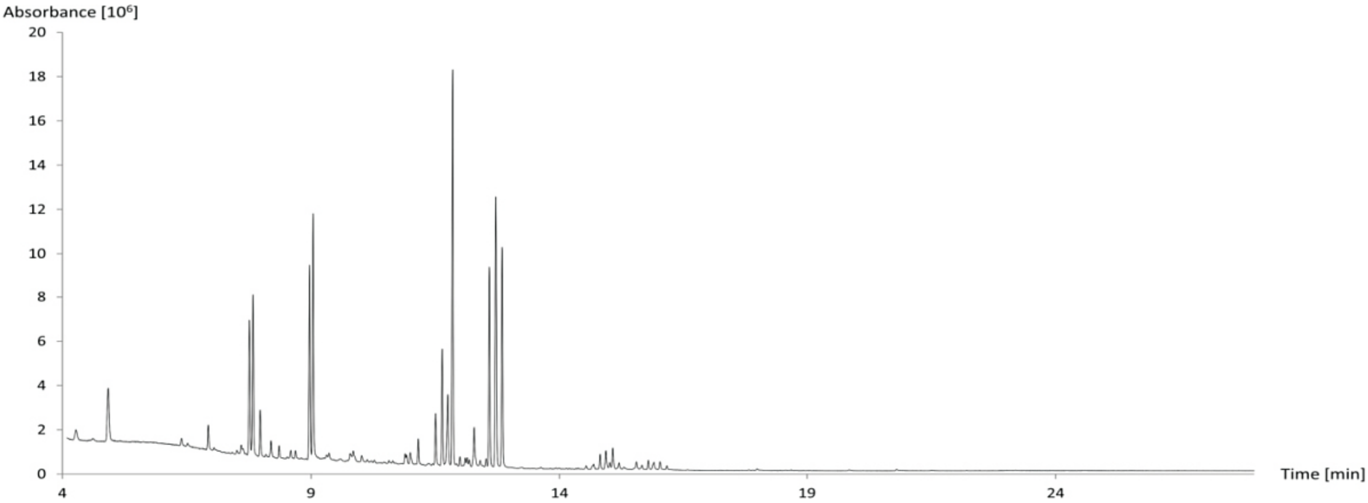

Figure C-9. Chromatogram from sample FXM000807. Conditions as in Figure C-8.

Table C-1. Compounds reoccurring across all samples analysed with the SPME method. Peaks identified in chromatogram from sample FXM000807.

Peak #	Ret Time (min)	CAS	Compound	RI	Ref RI
1	4.276	111-65-9	Octane	801	800
2	4.922	19549-87-2	2,4-dimethyl-1-heptene	841	842
5	6.935	17301-94-9	4-methyl-nonane	963	961
10	7.764	17302-28-2	2,6-dimethyl-nonane	1011	1022
11	7.835	17302-28-2	2,6-dimethyl-nonane	1015	1022
12	7.979	62338-48-1	7-methyl-4-decene	1024	1059*
18	8.973	13151-98-9	trans-1,4-dimethyl-cyclooctane	1081	1081*
19	9.044	13151-98-9	trans-1,4-dimethyl-cyclooctane	1086	1081*
31	11.508	61141-72-8	4,6-dimethyl-dodecane	1238	1285*
32	11.64	61141-72-8	4,6-dimethyl-dodecane	1246	1285*
33	11.754	61141-72-8	4,6-dimethyl-dodecane	1254	1285*
34	11.85	1014-60-4	1,3-bis(1,1-dimethylethyl)-bensene	1260	1334*
42	12.59	3913--02-8	2-butyl-1-octanol	1308	1393*
43	12.719	3913--02-8	2-butyl-1-octanol	1317	1393*
44	12.846	3913--02-8	2-butyl-1-octanol	1321	1393*

* Reference RI has been calculated theoretically.
Ret Time: Retention time, RI: Retention index, Ref RI: Reference retention index.

Arkitektkopia AB, Bromma, 2020

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