Institute for Energy Technology

DEUTERATED SHORT CHAINED FATTY ACIDS, A NEW CLASS OF ENVIRONMENTALLY COMPATIBLE RESERVOIR TRACERS

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Abstract

The chemical tracers used in petroleum reservoir characterization today are typically halogenated compounds, such as perfluorocarbons (gas tracers) and fluorinated benzoic acids (water tracers). In general halogenated compounds cause concern due to their impact on the environment. Having in mind the strict zero discharge requirement of the Norwegian Authorities it is necessary to provide new environmentally friendly tracers to the oil industry in order to reach this ambitious goal. Fatty acids are compounds, naturally present in petroleum reservoirs and due to their water solubility also traceable in the formation water. Due to the natural presence of deuterium in the environment also these fatty acids are to some minor extend deuterated. Hence fatty acids with a deuterium content above the natural level may act as water tracers in petroleum reservoirs.

Experiments performed have shown that

- It is possible to deuterate fatty acids at larger scale to reasonable costs
- These compounds survive under reservoir conditions
- Fatty acids act like water tracers

It is planned to inject a deuterated fatty acid during a field test within the near future. The intention of this contribution is to present this new concept and the results achieved so far.

INTRODUCTION

Tracer Technology, or with other words, the use of tagged molecules to monitor chemical, physical or technical processes is widely used by the petroleum industry to map the flow patterns in reservoirs, thus enhancing the reservoir description. At least two conditions

have to be fulfilled, before a substance can be accepted as a tracer: highly sensitive detectability and suitable chemical and physical properties to follow the traced fluid. For these reasons radioactive molecules have been (and still are) a natural choice when suitable tracers have to be found for a given tracer application. However, the number of suitable radioactive compounds is limited and their use is strictly regulated by national authorities. In consequence non-radioactive, or so-called chemical tracers have been developed. Many of these chemical tracers are halogenated or even perhalogenated. Today fluorinated benzoic acids (see Figure 1) are the most common chemical water tracers for reservoir applications.

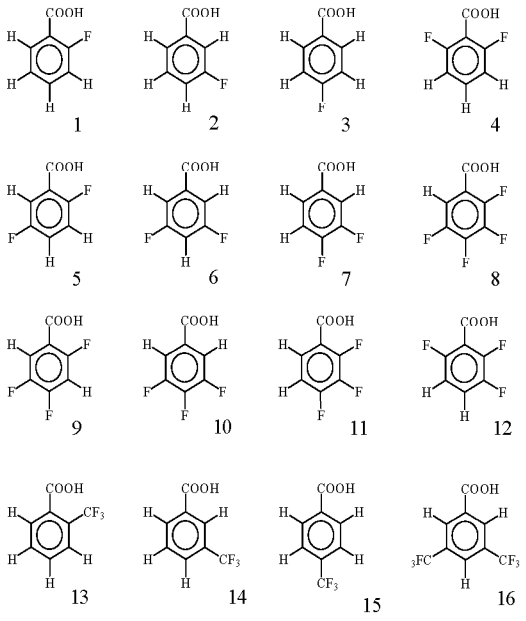

Figure 1: *Fluorinated benzoic acids, the most common chemical water tracers for reservoir applications*

The main function of the halogen atom(s) present in the molecule is to make the tracer distinguishable from those components naturally present in the petroleum reservoir. In many cases the halogen atom(s) make the chemical tracers also more resistant to biodegradation. Generally in Tracer Technology this is a positive effect. However from the environmental point of view compounds with too long biological half-lifes are not wanted. Thus there is an increasing need to find more environmentally friendly substances.

Fatty acids may act as such environmentally friendly tracers. They are naturally present in the reservoir and thus able to survive under reservoir conditions for a reasonable time. Tagged with deuterium, these acids are not radioactive, contain no halogen atoms and have still the same chemical properties as the natural homologues.

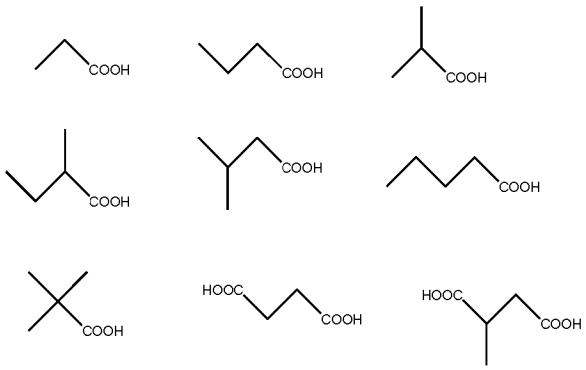

Figure 2: *The group of acids, investigated during the European " Envitracer" Research Project*

Provided that the number of deuterium isotopes in the molecule is large enough, it is possible to distinguish between the tracers and those molecules naturally present in the reservoir. Experiments performed during the Envitracer Research Project confirmed these assumptions:

- The investigated acids survive at reservoir conditions for at least 2 month.
- Dynamic flow experiments with tritiated water as the reference tracer demonstrated that the fatty acids behave like good water tracers.
- Based on GC/MS-techniques for the analysis of fluorinated benzoic acids analysis, methods for the determination of trace concentrations of deuterated fatty acids in aqueous reservoir matrices have been developed.

A drawback of this approach in developing environmental compatible reservoir tracers is the high costs of the commercial available deuterated compounds. Today deuterated compounds are mainly used as solvents or standards in analytical techniques such as nuclear magnetic resonance spectrometry (NMR) or mass spectrometry (MS). These techniques require minor quantities of such compounds in very high purity. But kg amounts of technical quality are required for reservoir tracer applications. At present, the

chemical industry is not prepared to supply this type of compounds in the right quality and quantities required for tracer use at reasonable prices. Pre-studies performed at IFE demonstrated that it is possible to produce deuterated compounds in tracer quality easily. The production of kg amounts of a deuterated tracer candidate for a pilot tracer injection in a North Sea Reservoir is scheduled for this year.

EXPERIMENTAL

Thermal Stability Tests

In order to evaluate the thermal stability of the tracer candidates a series of batch experiments has been carried out. Artificial Gullfaks brine was spiked with ppm concentrations of the candidates, filtered through a 0,45 µm filter and transferred to quartz ampoules. The quartz ampoules were carefully evacuated and sealed. Then the ampoules were placed in heating cabinets up to two month at 100 °C, 150°C, 175°C and 200°C. Finally the tracer concentrations were analyzed by HPLC and compared with a reference solution kept at ambient temperature.

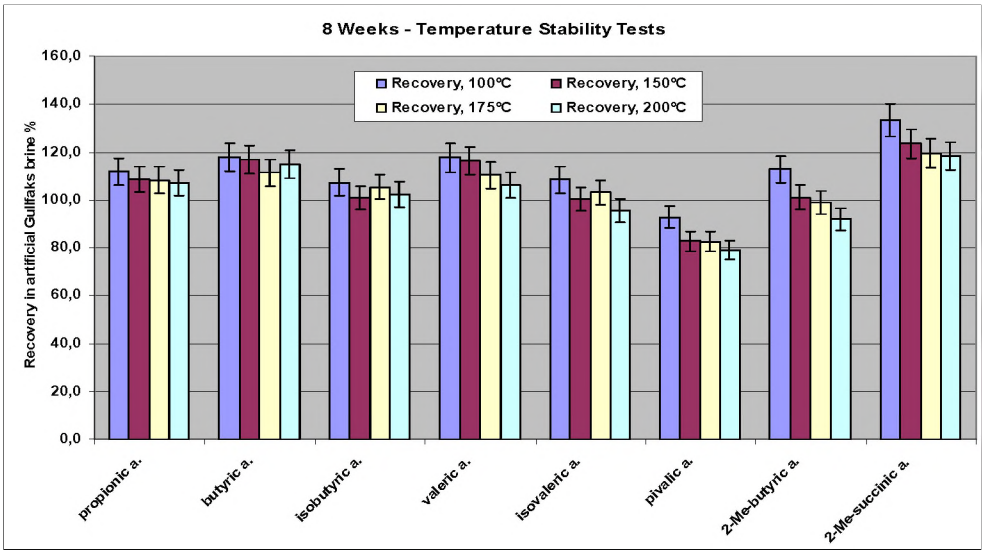

Figure 3: *Results from the eight weeks thermal stability tests in artificial Gullfaks brine.*

According to the diagram in Figure 4 all tracer candidates survive the eight week thermal stability tests at temperatures up to 150 °C with the exception of pivalic acid. Six of the candidates survive at 175 °C, while still five candidates survive 200°C.

Dynamic Flow Experiments

The mobility of the tracer candidates has been investigated in flow experiments both in core and column experiments. The column experiment has been performed with a flow-rig as shown in Figure 4. [1] The flow rig consists of a temperature controlled column, packed with crushed Berea sandstone, with a length of 2 m and an internal diameter of 11 mm. The pore volume of the column is typically about 80 ml. A residual oil saturation of 13 % was established prior to the flow experiments. The tracer candidates are mixed together with the reference tracer HTO, filled into a loop (250µl) and injected via a six-port valve onto the column. Typically seawater is used as the mobile phase. At the end of the column a fraction sampler takes 0,5 ml samples.

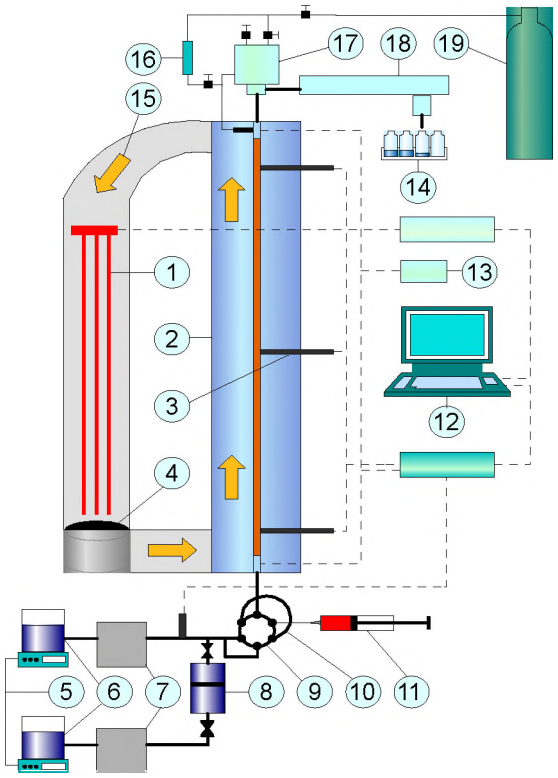

Figure 4: *Flow –rig for testing the flow behaviour of the tracer candidates: 1.Heating elements, 2.Isolated column compartment, 3.Thermo elements, 4.Fan, 5.Balance, 6.Mobile phases, 7. HPLC pumps, 8.Piston cylinder, 9. Six-port valve, 10.Injection loop, 11. Syringe, 12. Computer (Logging), 13. Differential pressure monitor, 14. Samples, 15. Circulating hot air, 16. Pressure equalizer, 17. Back pressure regulator, 18. Fraction sampler, 19. Nitrogen reservoir for dome pressure*

The HTO content in the fractions is measured by scintillation counting, while the concentration of the tracer candidates were determined by chromatographic techniques. The flow profiles of the candidates are compared with the profile of the reference tracer. Tracer response curves similar to the HTO profile indicate ideal water tracer properties. Figure 5 and Figure 6 show the tracer response curves of selected fatty acids. The measured concentrations are normalized to the peak concentration of each tracer

candidate. The Gaussian shape indicates that the tracers neither show partitioning to the oilphase nor show sorption to the rock material. The material balance confirmed that all tracers passed the sandstone column quantitatively. Thus, it can be concluded that the investigated tracers behave like ideal water tracers at the given experimental conditions.

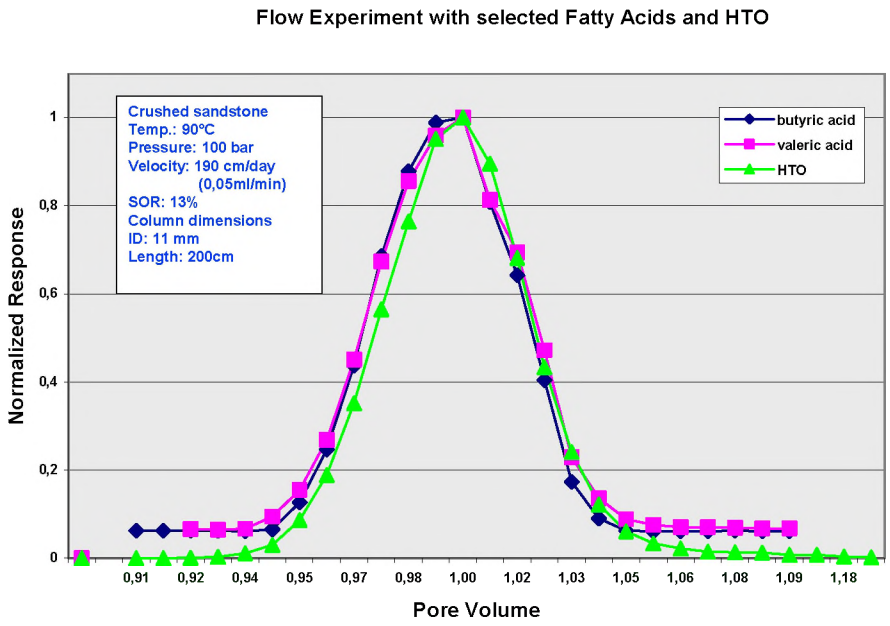

Figure 5: *Tracer response curves of selected fatty acids from a flow experiment carried out on a sandstone column with a residual oil saturation of 13%.*

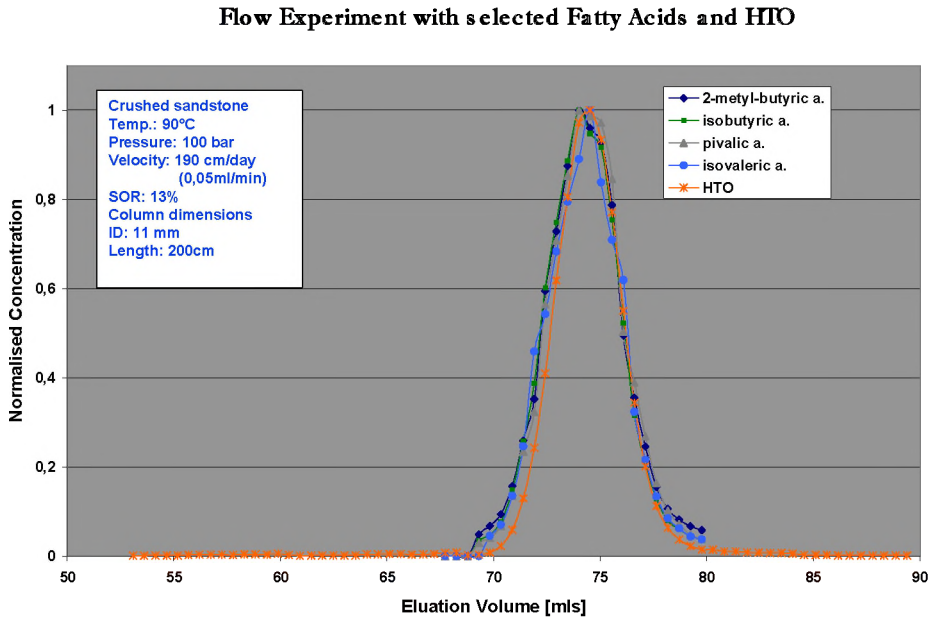

Figure 6: *Tracer response curves of selected fatty acids from a flow experiment carried out on a sandstone column with a residual oil saturation of 13%.*

The core experiment has been performed with an experimental set-up as shown in Figure 7. [2] The set-up consists of a high pressure cell, containing a Clashach sandstone core with a length of 7,3 cm and an internal diameter of 3,76 cm. The core is covered tightly with a hose. During the flow experiments a pressure above the pore pressure is applied to the pressure cell in order to keep the mobile phase inside the core. The pressure cell is placed into a heating cabinet for temperature control. Tracer injection and sampling, and pressure logging is performed similar to the experiments carried out on the flow-rig in Figure 4.

Figure 8 shows the results from the experiment carried out on a Clashach core with no oil in place. The experimental conditions are as indicated in the diagram. The selected tracer candidates show also in this experiment a flow profile similar to the reference tracer HTO, thus confirming their behaviour as ideal water tracers.

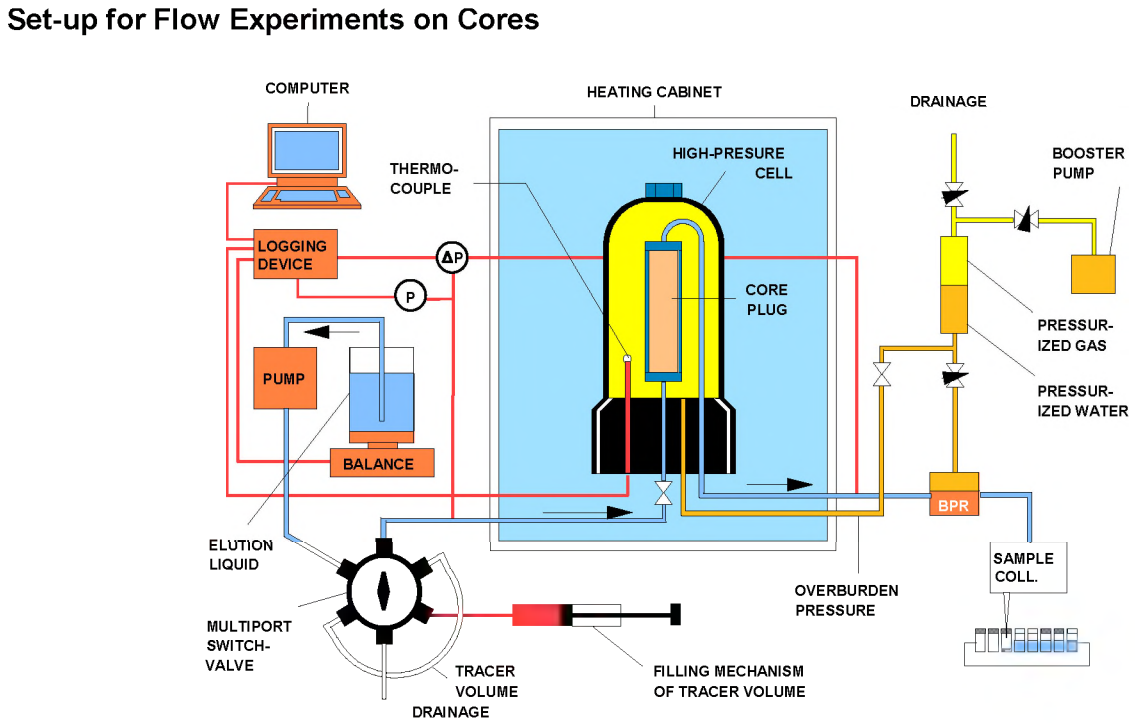

Figure 7: *Experimental set-up for flow experiments on cores*

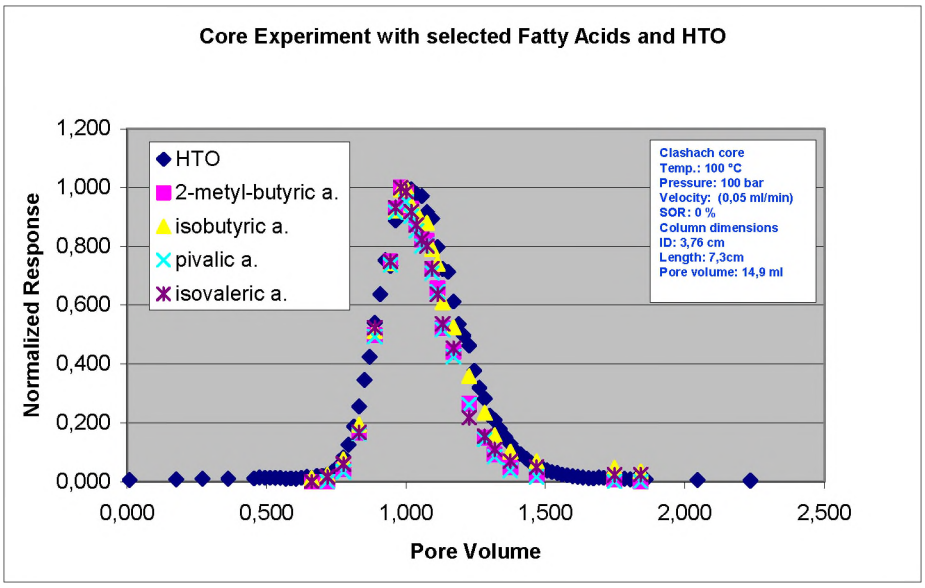

Figure 8: *Tracer response curves of selected fatty acids from a flow experiment carried out on a Clashach core with no oil in place. The mobile phase is artificial sea water*

Trace Analysis

The method for the analysis of trace concentrations of fluorinated benzoic acids in aqueous reservoir fluids [3,4] was adapted for the analysis of the actual tracer candidates. The analytical technique includes a sample preparation and pre-concentration step, followed by the derivatization of the carboxylic acids and the analysis by GC/MS. The sample preparation and pre-concentration step is carried out by utilizing solid phase extraction (SPE). The aqueous reservoir sample is filtered to remove particles and then adjusted to a pH of 1,5. At this low pH all fatty acids are protonated and adsorb to the polymer based sorbent material of the SPE cartridge. With a small volume of acetonitrile or a similar solvent the tracer candidates can be washed out of the cartridge. Careful evaporation of the solvent pre-concentrates the analytes further. An aliquot of the tracer concentrate is derivatized with diazomethane, or another suitable reagent. Finally the tracer soulution is analyzed by GC/MS. A diagram of the sample preparation procedure is shown in Figure 8 and the GC/MS parameters are shown in Table 1. Figures 9 & 10 show a typical chromatogram of the fatty acids and a mass spectrum of the pentafluorobenzylester of the perdeuterated valeric acid respectively.

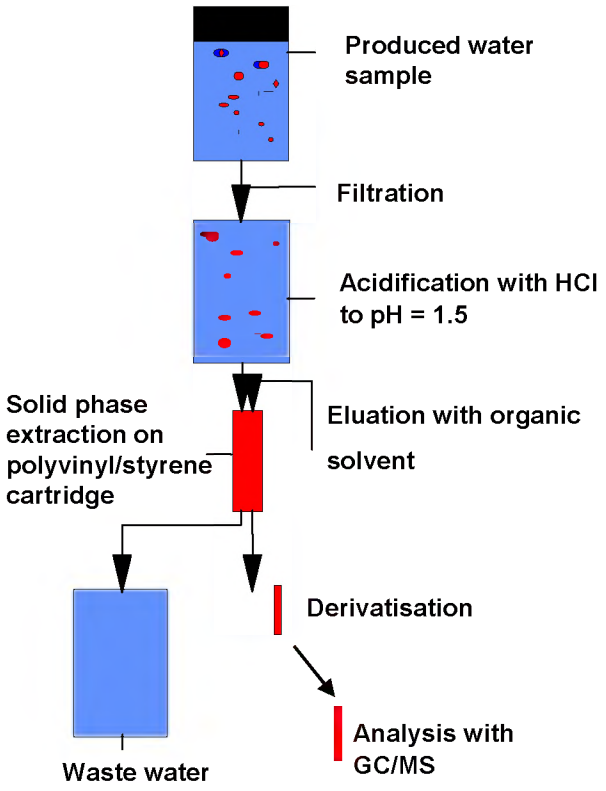

Figure 8: *A sketch of the analytical protocol for the trace analysis of the tracer candidates*

Sample preparation
Sample volume ca. 50 ml; polyvinyl/styrene SPE cartridges, derivatization with PFBBr
GC/MS parameter
Column: SGE HT-8; 50m x 0,22mm x 0,25µm
Injector temp. 260 °C GC/MS interface temp.: 320 °C
GC oven temp.program: 40°C in 2 min, then temp increase with 6 °C up to 200 °C and with 40 °C/min up to 300, then 300 °C in 6 min
Column head pressure: 24 psi, Injection vol.: 1 µl, Splitless injection,
Ion source temp.: 200 °C

Table 1: *Analytical conditions for the trace analysis of fatty acids*

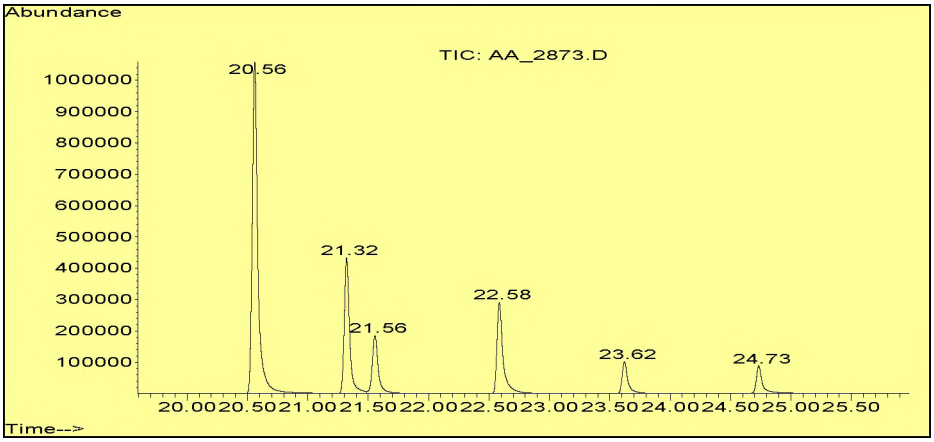

Figure 9: *A chromatogram of propionic acid, isobutyric acid, pivalic acid, butyric acid, isovaleric acid, valeric acid (in order of retention time)*

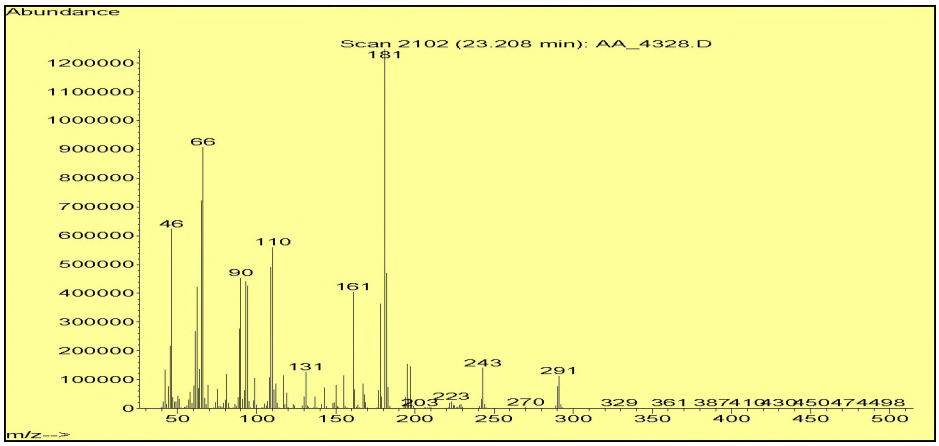

Figure 10: *A mass spectrum of the pentafluorobenzyl ester of the perdeuterated valeric acid. The molecule peak at m/z: 291 confirm the successful perdeuteration of the molecule (molecule peak for undeuterated valeric acid m/z: 282)*

Synthesis of Deuterated Fatty Acids

Deuterated compounds are used as standards in analytical techniques such as nuclear magnetic resonance spectrometry and mass spectrometry. These analytical techniques require high purity compounds where the position of the deuterium isotope(s) in the molecule in many cases has to be well defined. Together with the small quantities needed this is the reason for the rather high costs of the deuterated compounds commercially

available. For tracer purposes a technical quality with a well defined grade of deuteration above the natural level is sufficient. This can be achieved with a rather simple reaction.[5] The reaction equation (1) is valid for the deuteration of valeric acid (pentanoic acid).

$$(1)\quad CH_3CH_2CH_2CH_2COOH \xrightarrow[180°C,\ 7\ dager]{D_2O/NaOD/Pt} CD_3CD_2CD_2CD_2COOD$$

An excess of deuterium oxide is used as the deuterium source for the deuteration of organic acids. After the addition of the fatty acid the reaction mixture is neutralized with lye before a platinum catalyst is added. Then the reaction mixture is heated up to 180 °C for 7 days. Figure 11 shows the result of the deuteration reaction for valeric acid. The blue

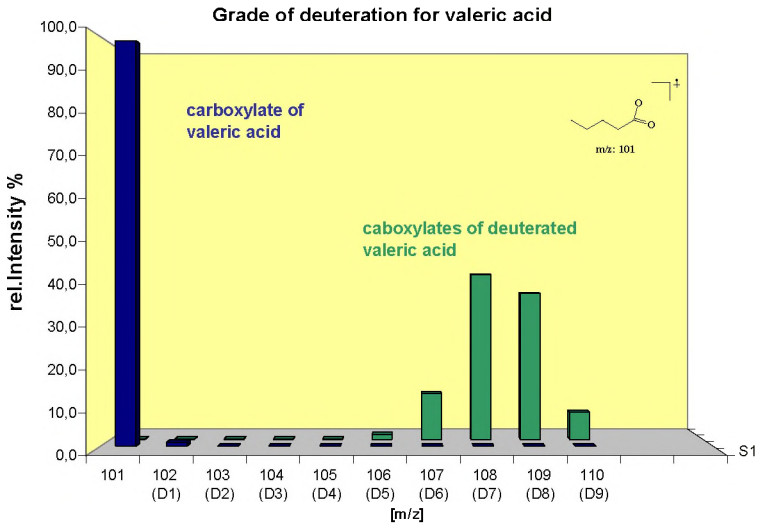

Figure 11: *The grade of deuteration for valeric acid achieved with reaction (1)*

column represents the mass of the carboxylate ion of the valeric acid before and the green columns the mass of the carboxylate ions after the deuteration reaction. The Figure shows that a sufficient number of deuterium isotopes has been introduced into the molecule to distinguish between the tracer and the acid naturally present in the environment. The continuation of the reaction for another week with fresh deuterium oxide, lead to an almost perdeuterated valeric acid, as shown in Figure 12.

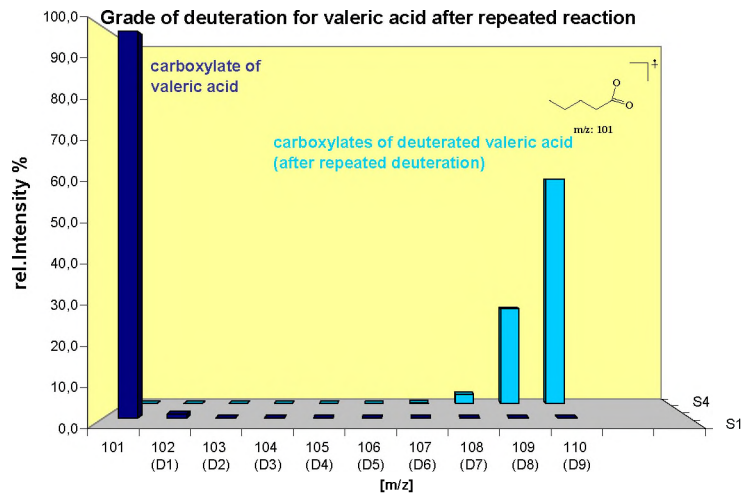

Figure 12: *The grade of deuteration for valeric acid achieved by running reaction (1) a second time*

The described reaction enables the easy introduction of deuterium isotopes into other fatty acids as well as many other organic molecules in a similar way.

CONCLUSIONS AND FURTHER WORK

Thermal stability tests have shown that five tracer candidates are stable for at least 2 month at 200 °C: propionic acid, butyric acid, isobutyric acid, valeric acid, 2-methyl-succinic acid. Another two candidates survive 2 month at 175°C: 2-methyl-butyric acid and isovaleric acid, while pivalic acid is not stable at elevated temperatures during this time frame.

Dynamic flow experiments performed under various conditions have shown that all investigated fatty acids have similar flow properties as the reference tracer HTO, thus confirming their behaviour as ideal water tracers under reservoir like conditions.

GC/MS methods, based on those developed for the fluorinated benzoic acids are available and make the determination of trace concentrations of selected fatty acids in aqueous reservoir fluids possible.

An easy way of introducing deuterium isotopes in fatty acids has been demonstrated. The described method enables the access to larger quantities of deuterated compounds for tracer purposes at reasonable costs.

A number of fatty acids have shown tracer properties in laboratory experiments. Sensitive analytical methods as well as a protocol for an easy deuteration of the tracer candidates are available. It remains to produce a necessary amount of a selected acid and inject the tracer in a North Sea Reservoir. Both activities are scheduled for 2006.

ACKNOWLEDGEMENTS

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