Development of new family of single well tracers

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Introduction

- Preliminary tests have been performed for development of a new family of single well tracers
- In the same way as ethyl acetate that has traditionally been used as single well tracer, the new tracers are based upon applying an ester that will hydrolyse after injection into the formation of a petroleum well
- After hydrolysis, the resulting acid and alcohol is back-produced and the concentration of the acid is measured in the produced water
- The tracer acid that is formed after hydrolysis of the new type of tracer, can be measured using high performance liquid chromatography with fluorescence detection (HPLC-FLD), and a detection limit of 1 ng/ml can be achieved
- The detection limit for the new tracer is in the order of 1000 times lower than can be achieved with the traditional ethyl acetate method, and the amount of tracer required for injection can therefore be reduced by the same factor
- The next three slides show chromatograms from test of partitioning to crude oil and test of hydrolysis rate for the suggested new single well tracer as well as detectability of tracer acid in produced water

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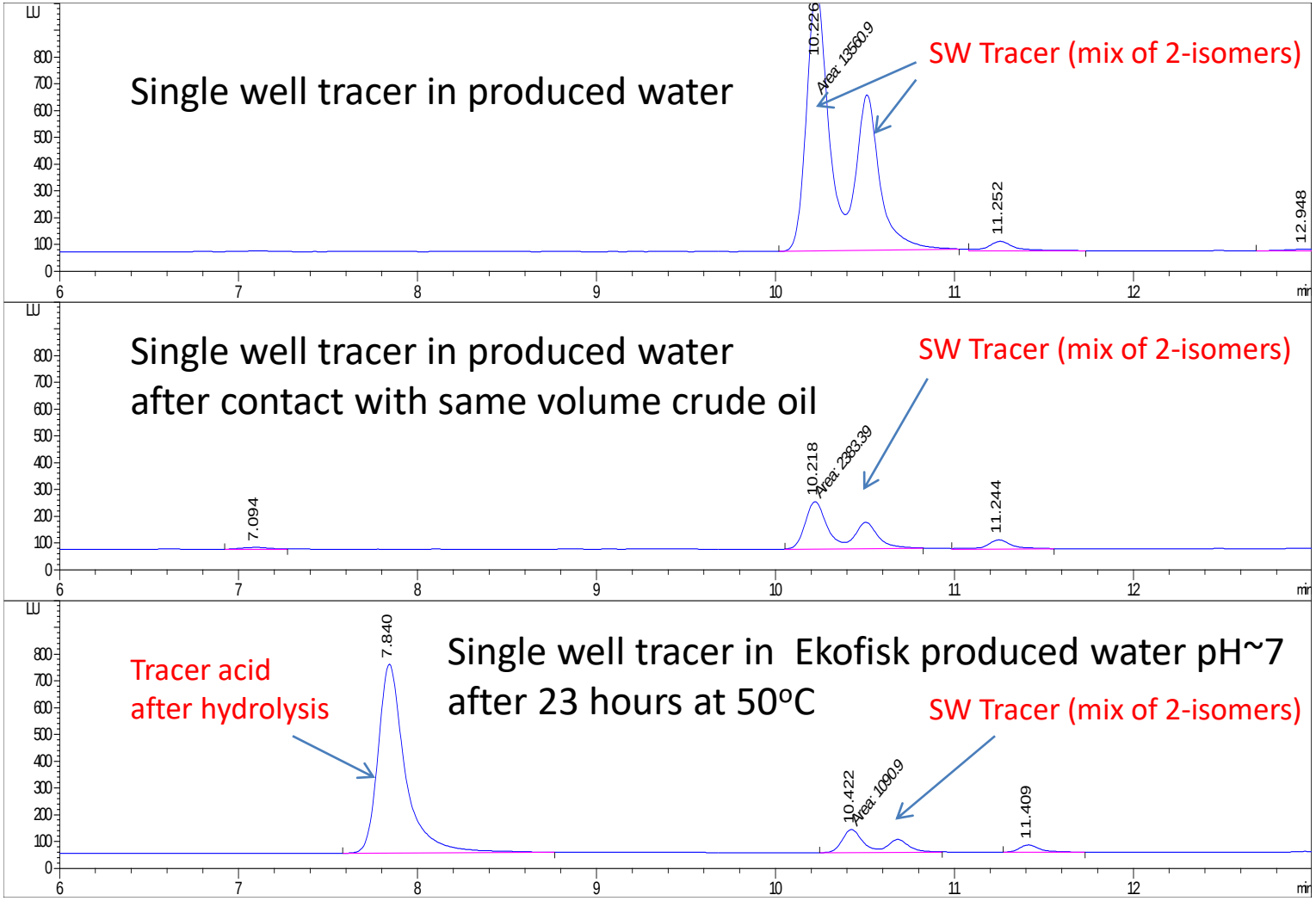
HPLC-FLD chromatograms from analysis of new single well tracer



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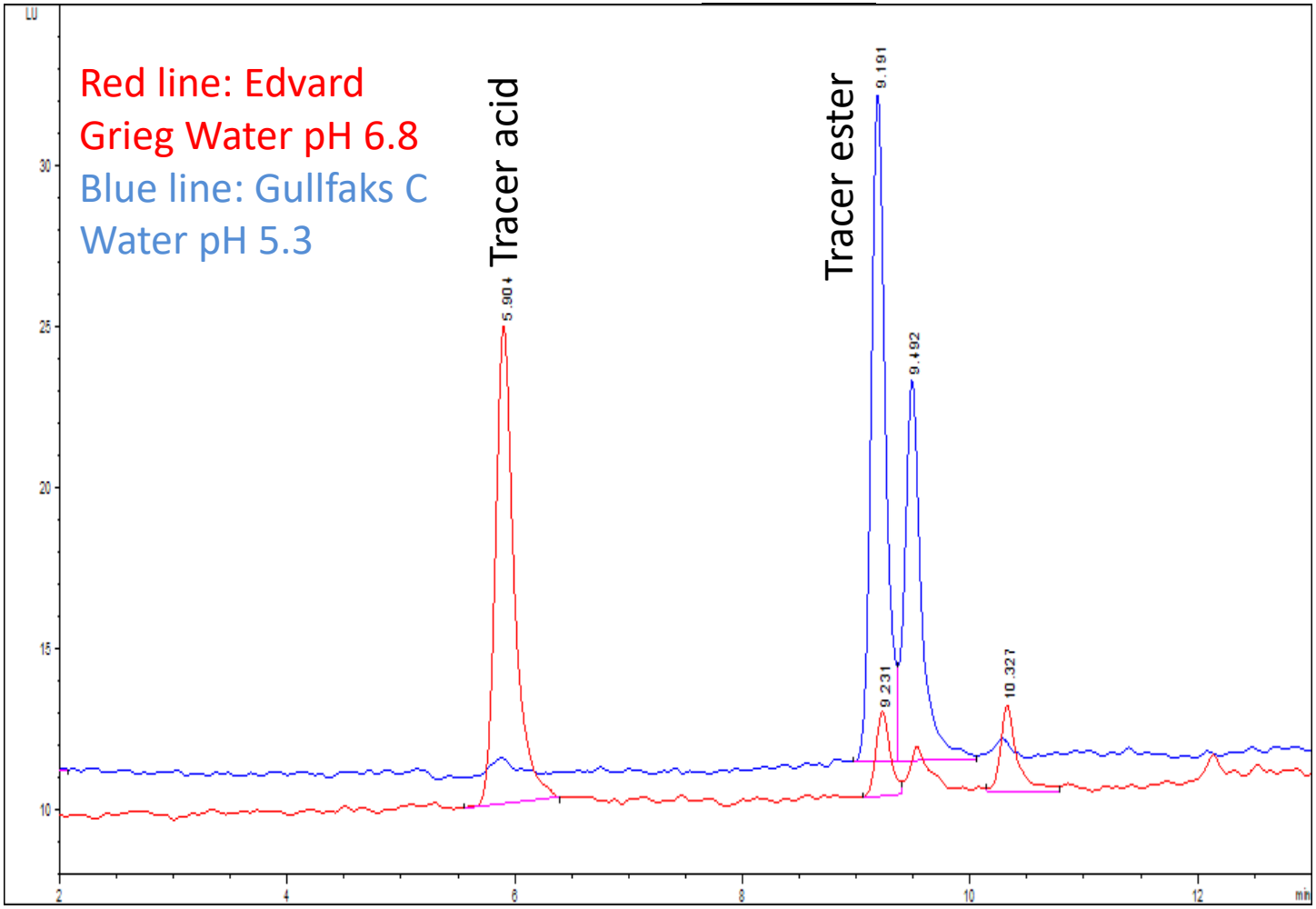
pH effect on hydrolysis rate after 20 hrs at 50°C



At pH 6.8 about 87% of the ester was hydrolysed
At pH 5.3 about 4% was hydrolysed

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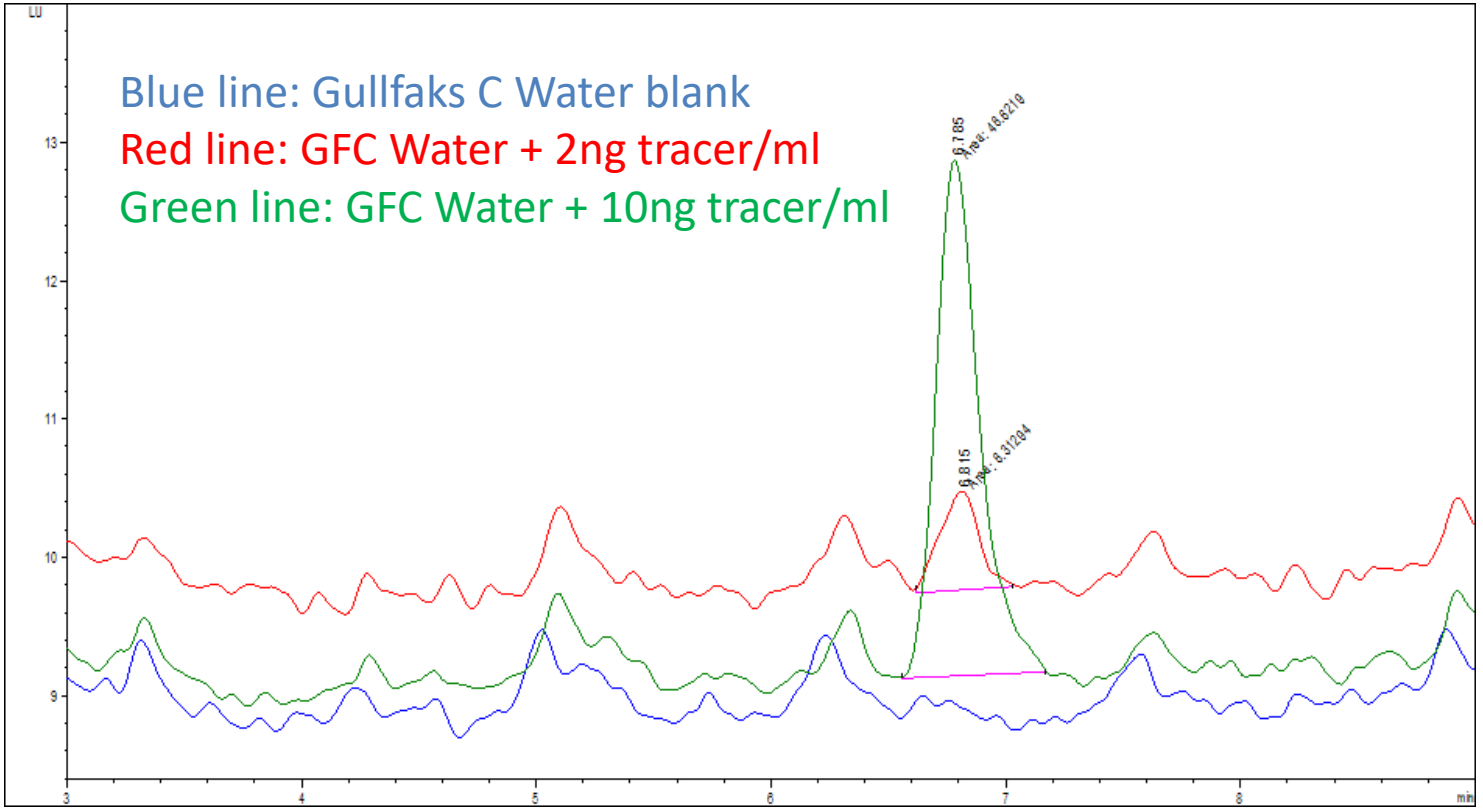
Detectability of the tracer acid



Estimated detection limit of tracer acid in Gullfaks C produced water without pre-concentration: 1ng/ml (ppb).

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Flooding experiment with sand packed column with and without crude oil

- A column with internal diameter 9 mm and 250 mm length was packed with sea sand
- 4% NaCl solution was pumped through the column at a flow rate of about 0.9 ml/min at ambient temperature (20^{o}C)
- 300 μl of a solution containing the tracer acid, the tracer ester and a passive water tracer was injected and fractions of the eluting solution from the column were collected every 30 second
- The same experiment was repeated after saturating the column with crude oil
- The fractions were analyzed by HPLC-FLD for the concentration of the tracer acid, the tracer ester and the passive tracer
- Elution profiles for the tracer acid, the tracer ester and passive tracer from the two experiments are shown in the next slides

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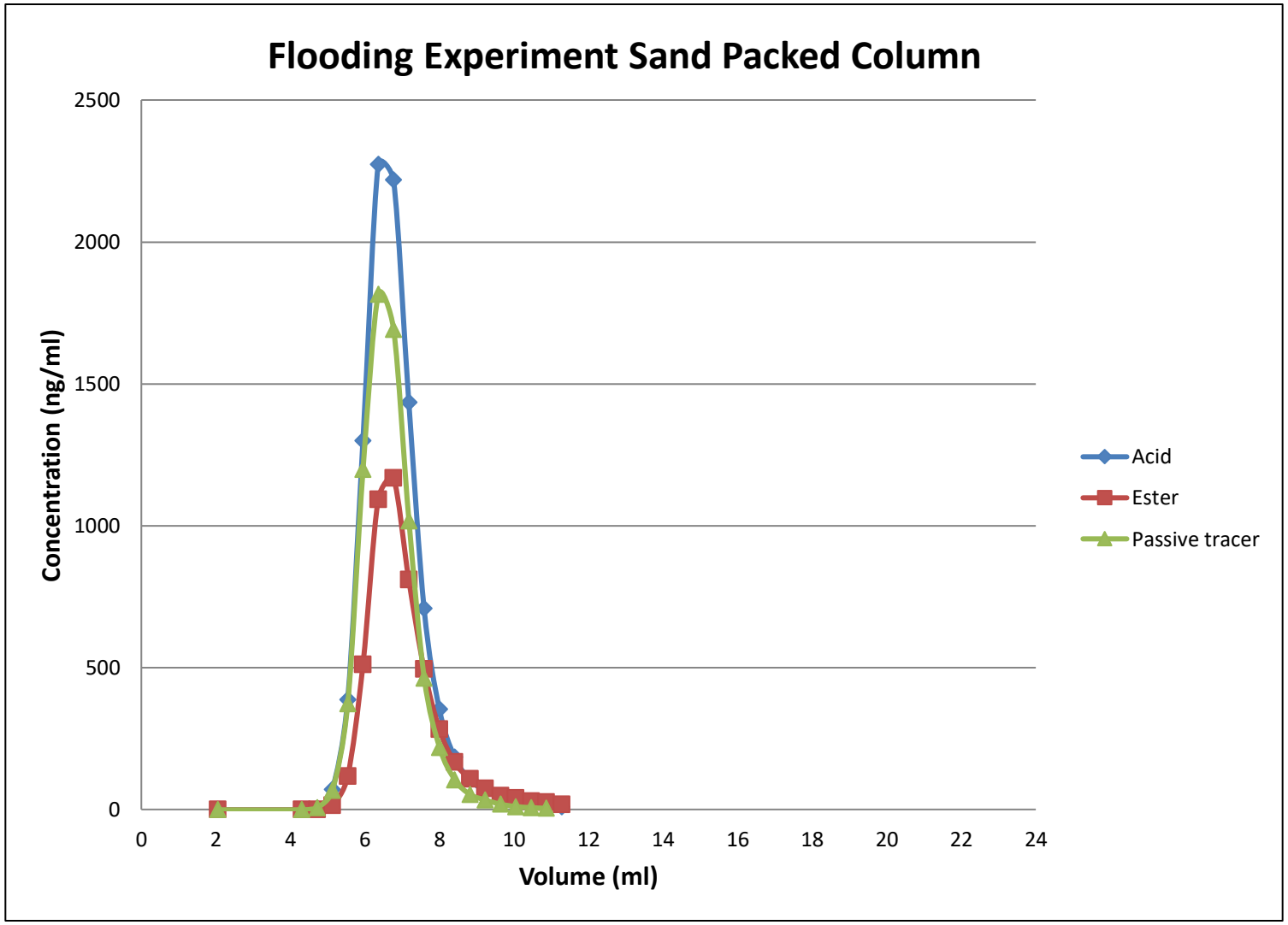

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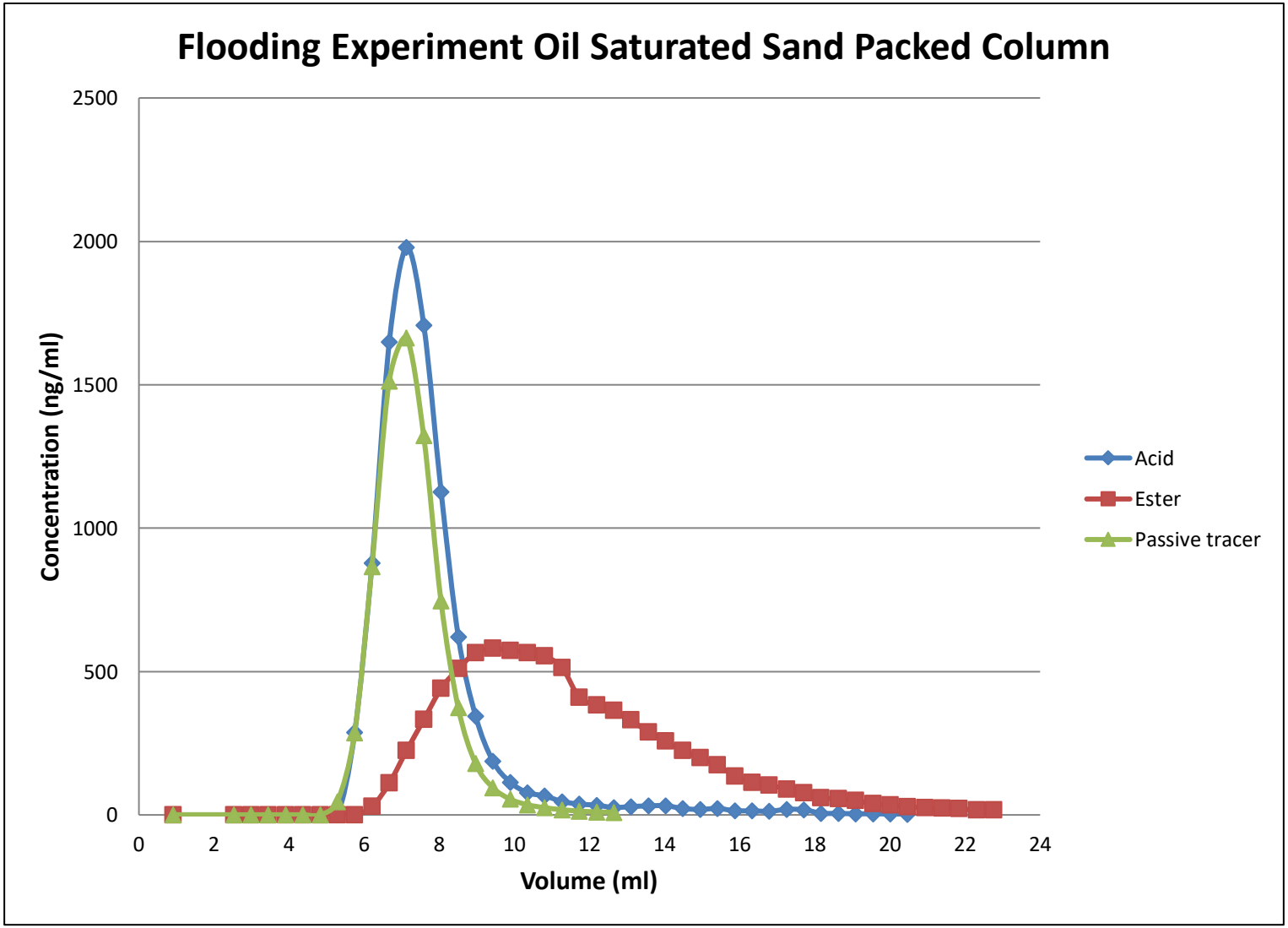

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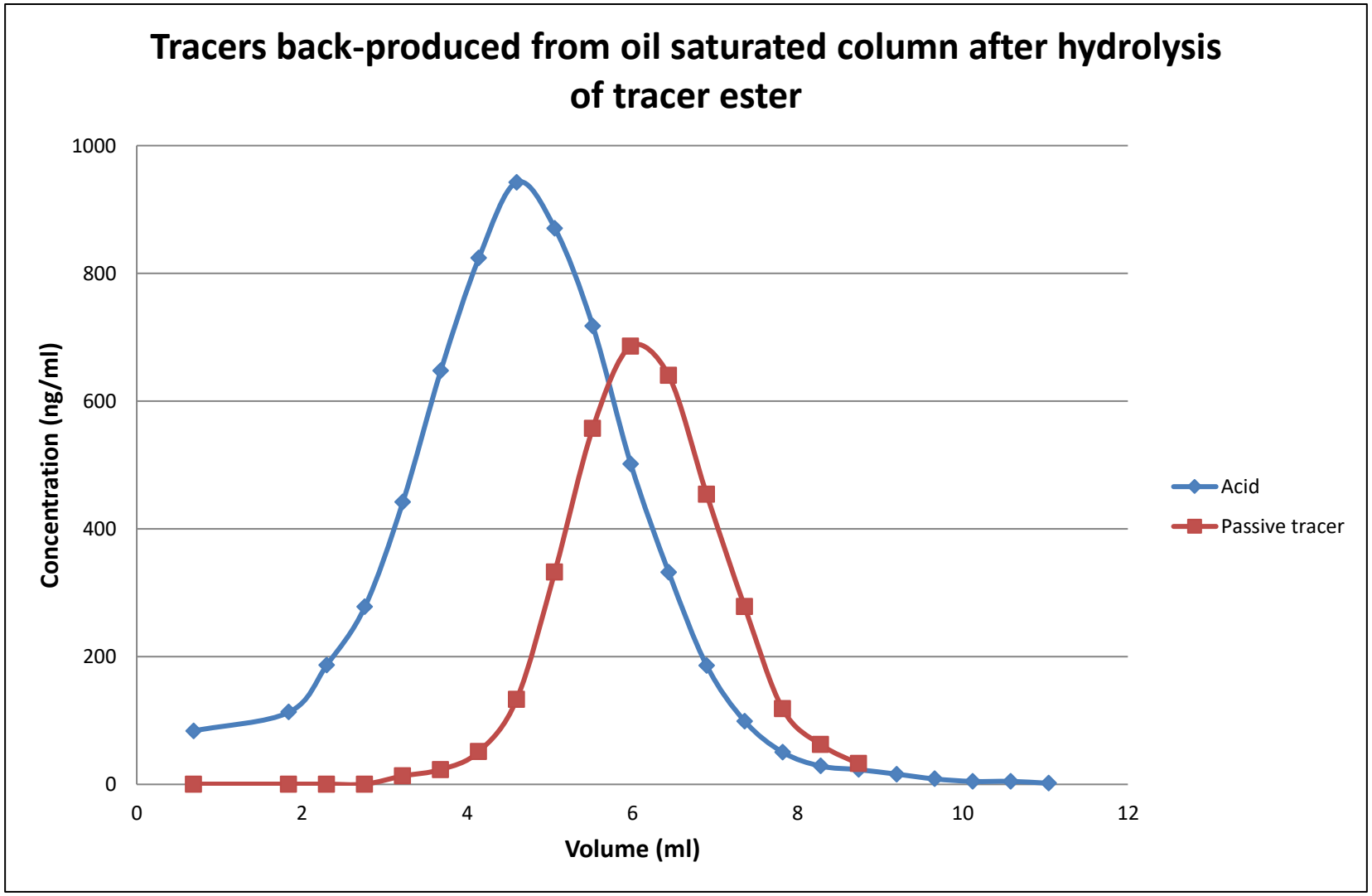
Experiment with back-production of tracers after hydrolysis of tracer ester

- The 9x250 mm column packed with oil saturated sand was also applied in the next experiment
- 4% NaCl solution was pumped through the column at a flow rate of 0.9 ml/min
- A solution containing the tracer ester and the passive tracer in 4% NaCl containing 0.1% H_3PO_4 was injected on the column and NaCl solution was pumped for 5 minutes until the passive tracerstarted to elute from the column
- The elution was stopped, the column was disconnected and plugged before it was placed in a heating oven at 60^oC
- After 20 hours the column was removed from the heating cabined and cooled to ambient temperature
- Elution was then restarted, but in the opposite direction, and fractions were collected first for 1.5 min and then for every 0.5 min
- The fractions were analyzed for the concentration of the tracer acid, the tracer ester and for the passive tracer
- The tracer ester was not observed in any of the 21 fractions
- The results for the tracer acid and the passive tracer are plotted in the next slide



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Conclusions

- The synthesized ester that was tested was mixed with Ekofisk produced water and the water was analyzed using HPLC-FLD
- A detection limit of about 1 ng/ml could be achieved after a simple clean-up and pre-concentration procedure
- Ekofisk produced water containing the tracer ester was mixed with equal volume of Ekofisk crude oil at 20^{o}C
- After centrifugation the water was again analyzed by HPLC-FLD
- From that experiment a K value of 4.7 was calculated
- A vial containing Ekofisk produced water spiked with the ester was put in a heating cabinet over night
- By analyzing the water before and after the heating period, it was found that after 23 hours at 50^{o}C 8% of the ester remained in the water sample, meaning that 92% of the ester had been hydrolyzed
- The pH of the Ekofisk produced water was relatively high (about 7). Tests of hydrolysis rate with other types of produced water with lower pH showed a much lower hydrolysis rate
- Earlier tests of thermal stability of the acid showed that it was stable for 24 hours at 60^{o}C in produced water
- The flooding experiments showed that the acid and the ester were not significantly retained compared to a passive tracer in a sand packed column. When the column was saturated with crude oil, the acid was eluted in nearly the same volume as the passive tracer while the ester was retained
- Back-production of the tracer acid after on column hydrolysis of the ester showed that the tracer acid was eluted earlier than the un-retained passive water tracer, indicating the suitability of the tracer ester as a single well tracer for estimation of oil saturation percentage in sediment layers of petroleum fields
- By applying this type of new tracer the danger of handling large volumes of the very flammable liquid ethyl acetate is avoided. The instrumentation applied for analysis is robust and affordable and is suitable for field applications