Determination of phase-partitioning tracer candidates in production waters from oilfields based on solid-phase microextraction followed by gas chromatography-tandem mass spectrometry

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A R T I C L E   I N F O

A B S T R A C T

In the present document, we report the development of an analytical method consisting of a sequential direct-immersion/headspace solid-phase microextraction (DI-HS-SPME) followed by gas-phase chromatography and tandem mass spectrometry (GC-MS/MS) for simultaneous analysis of 4-chlorobenzyl alcohol, 2,6-dichlorobenzyl alcohol, 4-methoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, pyridine, and 2,3-dimethylpyrazine in oilfield production waters. These compounds are under evaluation for use as phase-partitioning tracers in oil reservoirs. To the best of our knowledge, this is the first time SPME has been applied to the analysis of these compounds in production waters, or any other type of matrix where the compounds targeted are the base for a technical application. Relevant extraction parameters, such as the adsorbent phase of the fiber, direct immersion or headspace, addition of salt, temperature and time of extraction were investigated. The final optimal operation conditions consist on extracting 5 mL of sample at pH 9.0 with 1.8 g of NaCl with constant stirring during 5 minutes of DI-SPME followed by 15 minutes of HS-SPME at 70 °C using a DVB/CAR/PDMS (50/30 μm) fiber. The limits of quantification (LOQ), linearity, precision and accuracy of the method were evaluated. Analyses of the tracer compounds and recovery studies were also performed on production waters from 8 different oilfields of the Norwegian continental shelf. LOQs between 0.080 and 0.35 μg L^{-1} were obtained. The recovery yields of the method were consistently higher than 85% and RSDs less than 13%. None of the tracer compounds was found in the real samples processed, which is consistent with one of the requirements for an artificial tracer in an oilfield: absence or constant and low background in the traced fluid. The performance of the method developed, combined with its easiness to automate, introduce a new, accurate and cost-efficient technique to process the hundreds of samples required by an inter-well tracer test.

1. Introduction

Nowadays, tracer tests are routinely used by the oil industry to retrieve information about the reservoir. One type of such tests is the partitioning inter-well tracer test (PITT). A PITT measures the residual oil saturation (S_{OR}) in the flow path between injector-producer pairs in waterflooded oilfields [1–3]. S_{OR} is an important parameter for the conception and evaluation of improved oil recovery projects (IOR) in mature oil reservoirs, where conventional recovery processes fail to mobilize the remaining reserves of hydrocarbons. The average hydrocarbon recovery in conventional oil reservoirs is lower than 50% when production is stopped and large unexplored basins are located in remote and/or environmentally sensitive areas [4]. At the same time, projections from the International Energy Agency (IEA) indicate an increase of the global demand for fossil hydrocarbons until the year 2040 [5]. Satisfying the global demand for hydrocarbons requires further and efficient exploration of mature oilfields. Thus, the number of IOR projects has consistently been growing as well as the number of PITT which provide the data for them [6]. A PITT consists of the simultaneous injection of at least one passive tracer and one oil/water partitioning tracer that will travel the same flow path inside the reservoir. The partitioning tracer will be delayed relatively to the passive one due to an equilibrium distribution between the nearly stagnant hydrocarbon phase and the flowing

aqueous phase, and this delay is used to determine the hydrocarbon concentration [7,8]. The determination of the delay in the arrival of the partitioning tracers relies on the quantification of the tracer compounds often in several hundreds of produced water samples, collected during the test's timeframe, to build the tracer production curves. Low limits of quantification (LOQ) are desirable to increase the accuracy of these curves and also to reduce the amount of chemicals used in the test itself [9]. The growing attention on PITTs leads to a need for developing new oil/water partitioning tracers specifically qualified for this application in order to minimize the risk of unsuccessful field tests due to the use of inadequate tracer compounds [3,10]. 4-Chlorobenzyl alcohol; 2,6-dichlorobenzyl alcohol; 4-methoxybenzyl alcohol; 3,4-dimethoxybenzyl alcohol; pyridine; and 2,3-dimethylpyrazine were identified as relevant compounds in an ongoing comprehensive R&D project to introduce new oil/water partitioning tracers for the inter-well region of oil reservoirs [3,11,12]. Thus, an analytical method to identify and quantify these compounds in production waters from oilfields is required.

The analysis of organic compounds used as tracers in production waters from oil reservoirs is challenging and often requires several sample preparation steps. The sample preparation required to obtain acceptable LOQs typically involves an extraction/cleanup and concentration step using solid phase extraction (SPE), redissolution and, in some cases, derivatization [13,14] prior to analysis by GC-MS or LC-MS [15]. Although SPE is one of the most accepted and widely used sample preparation techniques [16], it is labor-intensive, time consuming and uses large amounts of solvents due to the high number of samples processed to complete the tracer test. In fact, the sample preparation step can be defined as the "bottleneck" of the analysis [17].

Solid-phase microextraction (SPME) is a mature, versatile, easy to automate, and solvent free sample preparation/concentration technique successfully used in a wide variety of applications with complex matrices, ranging from environmental analysis to clinical studies [18–20]. SPME fibers with several different adsorbent phases are commercially available. This is an advantage when considering the use of SPME in the processing of samples from PITTs. Standard and robust techniques are desirable to satisfy the large output of analysis required by the scope of this application. To the best of our knowledge, SPME has never been applied to the analysis of samples of production waters from oilfields. SPME has, however, been reported in the analysis of compounds from the same family of the compounds described in the present study. SPME was successfully used in the identification and quantification of benzyl alcohol [21–26], pyridine and pyridine derivatives [27–32] and substituted pyrazines [33–36] in aqueous, solid and gas matrices, and is also routinely used in the determination of volatile organic compounds in waste waters [37]. The extraction of analytes from aqueous samples using SPME is done either by direct immersion (DI-SPME) or by headspace extraction (HS-SPME). DI-SPME mode has been reported to be more efficient in the determination of less volatile oxygenated organic compounds leading, however, to a higher risk of fiber contamination or damage. HS-SPME mode is more indicated for more volatile analytes as it protects the fiber from such risks [37].

In the present study, we propose a methodology for analysis of the compounds identified as interesting PITT tracers in production waters from oilfields based on SPME-GC-MS/MS, with a sequential DI-SPME and HS-SPME extraction. This is the first report of the use of SPME in this matrix and we show that by introducing a sequential step of the two extraction modes (DI and HS), matrix interferences can be overcome and LOQs in the ng L^{-1} range achieved. The method presented has the potential to significantly reduce the time, labor and solvents used in the analysis of tracers in production waters. The developed methodology was applied to target the

tracer compounds in production waters from 8 different oilfields of the Norwegian continental shelf.

2. Experimental

2.1. Materials and reagents

4-Chlorobenzyl alcohol (99%), 2,6-dichlorobenzyl alcohol (99%), 4-methoxybenzyl alcohol (> 98%), 3,4-dimethoxybenzyl alcohol (99%), pyridine (≥ 99%) and 2,3-dimethylpyrazine (99%), manual SPME fiber holder, SPME fibers with coatings of CAR/PDMS (75 µm), PDMS/DVB (65 µm), DVB/CAR/PDMS (50/30 µm), PA (85 µm) and PDMS (100 µm), 10 mL SPME vials with aluminum screw caps with PTFE septa, and magnetic stirrers were purchased from Sigma-Aldrich (Sigma-Aldrich Norway AS, 0252 Oslo). Ultra-pure deionized water was obtained from tap water treated with a Milli-Q Advantage A10 system (Millipore, Burlington, MA, USA).

2.2. Instrumentation

The present study used a Thermo Scientific Trace™ 1310 gas chromatograph (Thermo Fischer Scientific, Waltham, MA, USA) equipped with a Restek Rtx®-5MS column (30 m X 0.25 mm X 0.25 µm) and coupled with a triple quadrupole mass spectrometer Thermo Scientific TSQ 8000 (Thermo Fischer Scientific, Waltham, MA, USA). The temperature program of the oven was as follows: initial temperature 50 °C kept for 3 minutes, followed by a ramp of 20 °C/min to 110 °C, and another ramp of 15 °C/min to 290 °C, and finally 7 minutes at 290 °C. Helium with a purity of 99.999% (Praxair Norway AS, 0663 Oslo) was used as carrier gas at a constant flow of 1 mL/min. The temperature of the injector was 250 °C and the temperatures of the ion transfer line and ion source were 290 °C and 320 °C, respectively. The injector was operated in splitless mode for 2 minutes returning to split mode after this time. The mass spectrometer (MS) was operated in electron impact (EI) ionization mode (+70 eV) and selected reaction monitoring (SRM) was used to monitor specific transitions for each of the target compounds presented in Table 1. The operation conditions of the MS were previously optimized for the target compounds.

2.3. Field samples

1 L of production water samples from 8 different oilfields on the Norwegian continental shelf were obtained from the respective operators. The oilfields in question were as follows: Snorre A, Snorre B, Ekofisk M, Gullfaks C, Heidrun A, Eldfisk A, Eldfisk S and Vigdis B. These are fields close to maturity that have been under water flooding conditions for many years. Typical ranges for several physicochemical parameters of produced waters from oil reservoirs can be found in published literature [38].

2.4. Experimental procedure

2.4.1. Selection of the type of SPME fiber and preliminary tests

1L of individual solutions of each of the target compounds with a concentration of 10 µg/L were prepared in ultra-pure water. The pH of the solution was adjusted to 9.0 ± 0.1 to prevent protonation of the pyridine, with sodium hydroxide 0.05 M and measuring the solution under constant stirring using a pH meter. 5 mL of solution were transferred to the SPME vials and 1.8 g of NaCl were added. The solution was stirred on a magnetic stirrer at 80 rpm for a minimum of 5 minutes before thermal incubation. Increasing the salinity of the matrix is a well-known technique to facilitate the extraction of organic compounds in solution [39], however extractions without any added NaCl were also performed. All SPME fibers were conditioned prior to use according to the instructions of the

Table 1
Experimental GC-MS/MS parameters for the target compounds and some physico-chemical properties.

Compound	Acronym	MW[a] (g mol^{-1})	VP[b,c] (mTorr)	log k$_{ow}$[b,d]	Ret. time (min)	MS/MS transitions (identification)	MS/MS transitions (quantification)	CE (eV)
Pyridine	PYR	79.04	19.3×10^3	0.65	5.89	$52 \rightarrow 39$ $79 \rightarrow 52$	$79 \rightarrow 52$	30
2,3-Dimethylpyrazine	23MPRZ	108.07	2.74×10^3	0.54	6.41	$40 \rightarrow 39$ $67 \rightarrow 52$ $108 \rightarrow 93$	$108 \rightarrow 93$	25
4-Chlorobenzyl alcohol	4BZOH	142.02	0.268	0.82	14.13	$77 \rightarrow 75$ $107 \rightarrow 90$ $142 \rightarrow 125$	$142 \rightarrow 125$	20
2,6-Dichlorobenzyl alcohol	26BZOH	175.98	0.254	1.07	14.82	$113 \rightarrow 77$ $141 \rightarrow 123$ $176 \rightarrow 159$	$113 \rightarrow 77$	20
4-Methoxybenzyl alcohol	4METBZOH	138.07	0.082	0.71	16.47	$109 \rightarrow 95$ $121 \rightarrow 90$ $138 \rightarrow 107$	$138 \rightarrow 107$	25
3,4-Dimethoxybenzyl alcohol	34METBZOH	168.08	0.0696	0.62	17.27	$139 \rightarrow 95$ $151 \rightarrow 120$ $168 \rightarrow 137$	$168 \rightarrow 137$	25

[a] molecular weight.
[b] properties calculated using the US Environmental Protection Agency's EPISuite™.
[c] vapor pressure at 25 °C.
[d] octanol/water partition coefficient.

manufacturer. The extraction with the different SPME fibers was performed manually under constant stirring at a fixed temperature of 50 °C for 30 minutes, both in direct immersion and headspace modes. Three replicas were used for each test standard. The mean value of the chromatographic areas was used to choose both the most appropriate adsorbent phase and SPME extraction mode.

2.4.2. Optimization of the conditions of SPME extraction

A sample of real production water (Ekofisk M) was used to optimize this approach together with the selected SPME fiber. This sample was selected because it presented the highest contamination of hydrocarbons upon visual inspection. The sample was spiked with a mixture of the tracer compounds (4BZOH, 26BZOH, 4METBZOH, 34METBZOH, PYR, and 23MPRZ) at a concentration of 10 μg/L. The pH was adjusted to 9.0 ± 0.1 and 5 mL were transferred into SPME vials. Again, constant stirring was used during the whole extraction period. The time and temperature of extraction were evaluated between 5 - 40 minutes and 30 – 90 °C, respectively, as well as different periods of DI and HS combined. This procedure intended to maximize the signal obtained from the analysis of the analytes while simultaneously preventing interference effects from the matrix. DI should increase the extraction yield of the compounds with lower volatility (4METBZOH, 34METBZOH). After the extraction and before insertion in the injector port, the SPME fiber was conditioned during 2 minutes in ultra-pure water to preserve the chromatographic system. The desorption time for the fiber in the injector port was set to 10 minutes.

2.4.3. Validation of the method

Using the optimized conditions of the method, limits of quantification and detection (LOQ and LOD) were determined at the concentration level for a signal to noise ratio (S/N) of 10 and 3, respectively. The linearity was evaluated from the coefficient of determination by preparing a calibration curve and using r ≥ 0.995. To validate the obtained range, a standard residual analysis was performed as described by Eurachem [40]. The recovery was evaluated in all the 8 different available samples, spiked with known amounts of the analytes, and calculated using Eq. 1

$$\%Recovery = \frac{Determined\ analyte\ concentration}{Expected\ analyte\ concentration} \cdot 100 \qquad (1)$$

Intra-day and inter-day precision were evaluated at 3 different concentration levels (low range, middle range, and high range)

with 7 and 5 replicates per level for intra-day and inter-day, respectively.

3. Results and discussion

3.1. Selection of the adsorbent SPME phase and preliminary tests

The fixed conditions of time and temperature of extraction described in Section 2.4.1. allowed for a direct comparison between extraction modes (DI and HS) and to evaluate the impact of increased salinity on the efficiency of extraction, often described as key factor when SPME is used as sample preparation technique. For these tests, standard solutions of the individual target compounds in deionized water were used and the resulting average chromatographic areas (n = 3) for each compound are presented in Fig. 1. Extraction of every compound in both DI-SPME and HS-SPME modes was observed using 3 adsorbent phases (PDMS/DVB, CAR/PDMS and DVB/CAR/PDMS).

Results indicate that the PA SPME fiber fails to extract PYR, 23MPRZ, 4METBZOH and 34METBZOH in both DI and HS modes, while the PDMS fiber fails to extract 4METBZOH and 34METBZOH in HS mode. The target analytes have a significant affinity for lipophilic phases, as deduced from their log K$_{OW}$ values (see Table 1). Polyacrylate is a linear polymer with polar groups. The polar interactions from these groups are likely not strong enough to disrupt the interactions between the water molecules and induce the partitioning of PYR, 23MPRZ, 4METBZOH and 34METBZOH to the adsorbent phase, without the presence of a highly lipophilic chain. Thus, this is the possible reason why the PA SPME fiber fails to extract PYR, 23MPRZ, 4METBZOH and 34METBZOH. DI extraction mode improves the response relatively to HS for every compound and fiber used. This is particularly observable for 4METBZOH and 34METBZOH, the compounds with lower volatilities (see Table 1), and the global results are in general agreement with what could be expected when this property of the target analytes is considered, as they will be available for adsorption to the fiber in lower amounts in the headspace. The addition of 1.8 g of NaCl has a positive effect on the efficiency of extraction in both DI and HS modes for all the analytes (see Fig. 1). Improvements in the efficiency of extraction are particularly observed for the chlorinated benzyl alcohols, whose volatility is significantly impacted by the salinity of the aqueous matrix. The salting-out effect makes
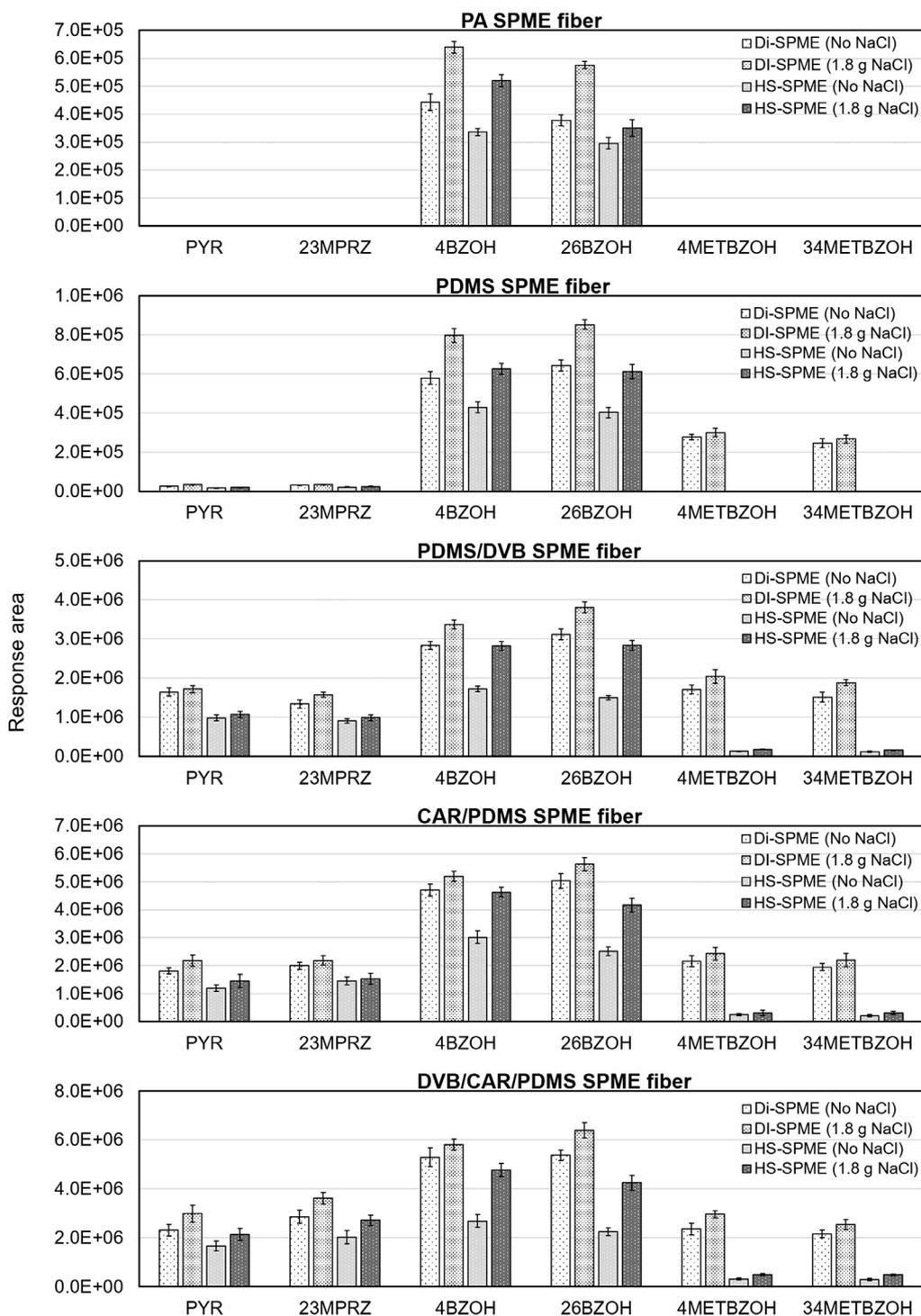
Fig. 1. Response areas for each of the target compounds in solutions of 10 μg/L extracted with the different SPME fibers for 30 minutes at 50 °C and effect of addition of NaCl.

them available in higher concentration in the vapor phase. The SPME fiber with the adsorbent phase DVB/CAR/PDMS produced the best results (slightly larger peak areas than CAR/PDMS) for every analyte in both extraction modes and was therefore selected for the rest of the study. Both the DVB/CAR/PDMS and CAR/PDMS fibers are often referred to as a "bi-polar" adsorbent phases, as they contain polar groups and non-polar groups. The possibility of polar and non-polar interactions with the analytes, increases their partitioning to the SPME fiber, resulting in higher efficien-

cies of extraction. The fact that DVB/CAR/PDMS yields better results is likely due to an additional partition effect induced on the analytes by the benzene rings present on coating of the fiber. All the target compounds of the present study have either benzene rings or benzene-like cyclic structures. A DI-SPME extraction mode combined with the addition of 1.8 g of NaCl was initially considered, as the preliminary results suggested this approach to maximize the efficiency of extraction of all the 6 target tracer compounds.
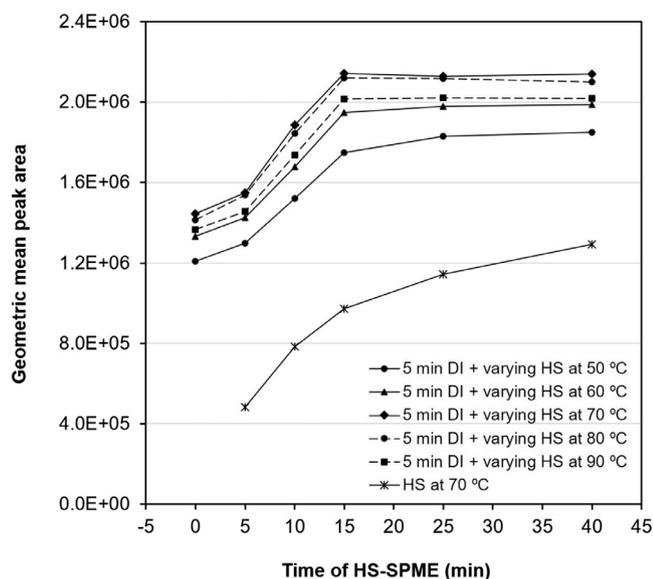
Fig. 2. Geometric mean response area of the target compounds as function of the time and temperature of HS-SPME extraction after a fixed DI-SPME period of 5 minutes.

3.2. Optimization of the conditions of SPME extraction

The study to optimize the temperature and time conditions for a DI-SPME extraction with the DVB/CAR/PDMS fiber was initiated on a mixed standard solution of all 6 compounds in deionized water with a concentration of 10 µg/L. Because real production waters are complex matrices, tests were made to assess their influence on the performance of the extraction. We found that interferents could compromise the detectability of the compounds when prolonged DI extraction periods were used. If purely HS extraction was employed, the efficiency of extraction, particularly of the less volatile compounds (4METBZOH and 34METBZOH) would, on its turn, be severely reduced. Thus, a sequential DI-HS extraction was considered, and the maximum DI extraction time was evaluated to maximize the signals of the analytes without compromising their detectability due to interferences. An aliquot of the 8 different oilfield production waters was spiked with 10 µg/L of the tracer compounds and DI-SPME was performed for different periods of time. We verified that in the worst-case scenario (production water from Ekofisk M), about 6.5 minutes of DI-SPME would start compromising the detectability of the tracers. A sequential DI-HS-SPME extraction procedure with a fixed time of DI-SPME of 5 minutes was adopted to maximize as much as possible the measured responses for the analytes while simultaneously eliminating the risks of matrix interference. The time of HS-SPME was then optimized together with the temperature of extraction using production water from Ekofisk M spiked with 10 µg/L of the tracer compounds and with 1.8 g of NaCl added. Fig. 2 presents the geometric means of the areas of the compounds of interest as function of temperature and time of HS-SPME (with a fixed DI-SPME period of 5 minutes).

Results indicate that the maximum extraction efficiency is achieved with 15 minutes of HS-SPME extraction performed after 5 minutes DI-SPME at 70 °C. The response areas obtained at this temperature are very similar to the ones obtained at 80 °C and an argument can be made that there are no significant differences between them. Because the results are so similar at these two temperatures and a slightly more elevated trend of values can be argued for in the results at 70 °C, this was the temperature adopted for the rest of the study. SPME is not an exhaustive ex-

traction technique and the equilibrium of the system was achieved after a relatively short period of 20 minutes (5 minutes of DI + 15 minutes of HS) of extraction (except when extraction is done at 50 °C). This is most likely due to a combined effect of temperature and the initial step being DI-SPME. Initiating the sequential extraction procedure with DI maximizes the mass transferring gradient between the bulk of the sample and the SPME fiber, thus maximizing the velocity of adsorption. Increasing temperature will increase the volatility of the analytes and promote their fastest transfer to the headspace once the equilibrium between it and the bulk of the sample is disturbed by the HS-SPME extraction. It should be noted that this is true until an upper temperature value. The results show that the efficiency of the SPME extraction decreases at a temperature of 90 °C. This can be explained by the reduction of the adsorption capacity of the SPME fiber as consequence of an excessively high temperature of operation which promotes some desorption.

The final optimized SPME extraction procedure was as follows: 1.8 g of NaCl were added to an aliquot of 5 mL of sample at pH 9.0 ± 0.1. The sample was kept under constant stirring and extracted at 70 °C with a sequential DI-HS-SPME consisting of 5 minutes of DI and 15 minutes of HS.

3.3. Chromatographic analysis

SPME extracts many other compounds from the real produced water samples in addition to the target analytes. Fig. 3 shows a total ion chromatogram (TIC) (35-800 m/z) recorded from the sample of produced water from Ekofisk M spiked with the tracer compounds at a concentration of 10 µg L^{-1}.

The result is a fairly complex chromatogram where the identification of the tracers is not clear at first sight, however the major ions of the EI spectra of all compounds may still be identified at their respective retention times (see Table 1). Using the triple quadrupole under tandem/MS conditions allows optimizing selectivity and sensitivity reducing the noise in the measured responses. Additionally, timed data acquisition was used to further enhance these parameters. The MS was operated in selected reaction monitoring (SRM) mode and three transitions per compound were monitored to ensure the identification of the analytes in combination with the respective chromatographic retention times. These were further used to define the periods for data acquisition by the MS. The operating conditions of the GC and the MS were previously optimized and information about the chromatographic retention times, collision energies, and transitions for identification and quantification are presented in Table 1. Fig. 4 displays a reconstructed SRM chromatogram obtained from a sample of production water from Ekofisk M spiked with the tracers at a concentration of 1 µg L^{-1} and extracted with the optimized senquential DI-HS-SPME procedure.

3.4. Evaluation of the performance of the method

The linearity, precision, accuracy, and recovery of the DI-HS-GC-MS/MS method were evaluated. The limits of quantification (LOQ) and limits of detection (LOD) were calculated as the concentration of the compounds originating a signal to noise ratio (S/N) of 10 and 3, respectively, by applying the optimized analytical method to real samples spiked at varying low concentrations. We verified that the concentrations of the analytes which originate S/N ≥ 10 are systematically lower than the lower linear concentration threshold. LOQ and LOD values are indicated in Table 2. Because the present method is conceived for an application where the processing of a large number of samples is required, the use of the lower limits of linearity as LOQ is recommended for systematic analysis.
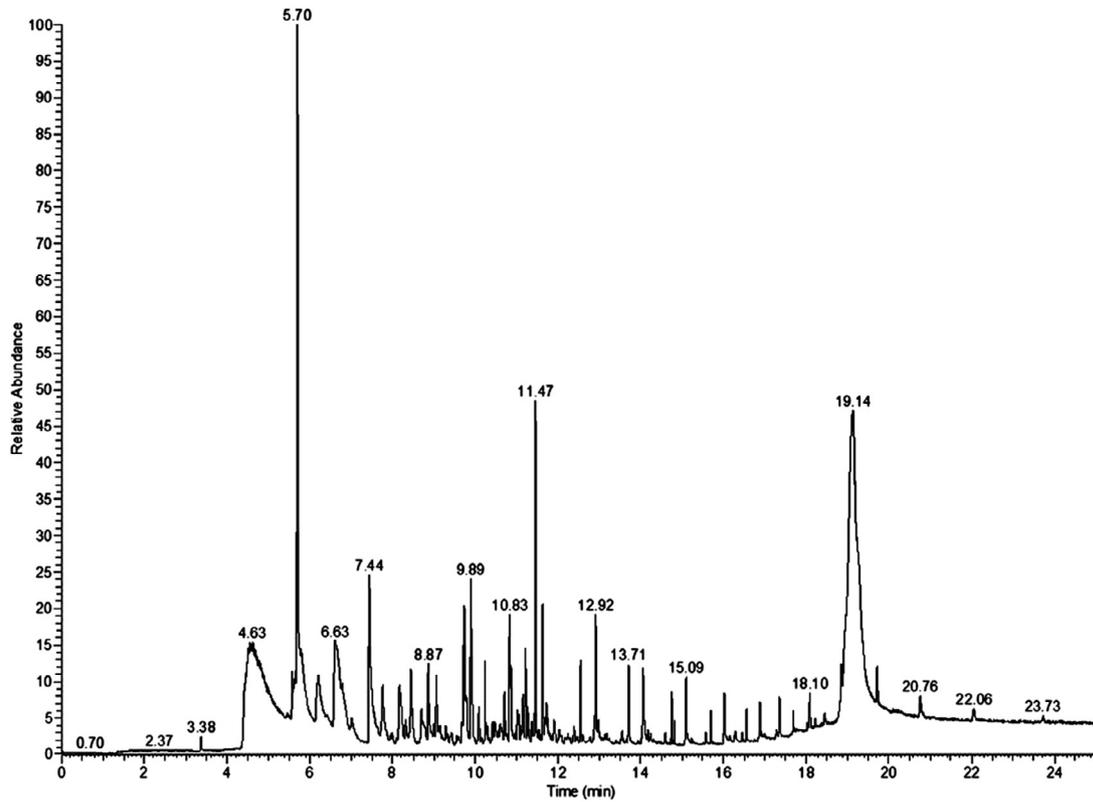
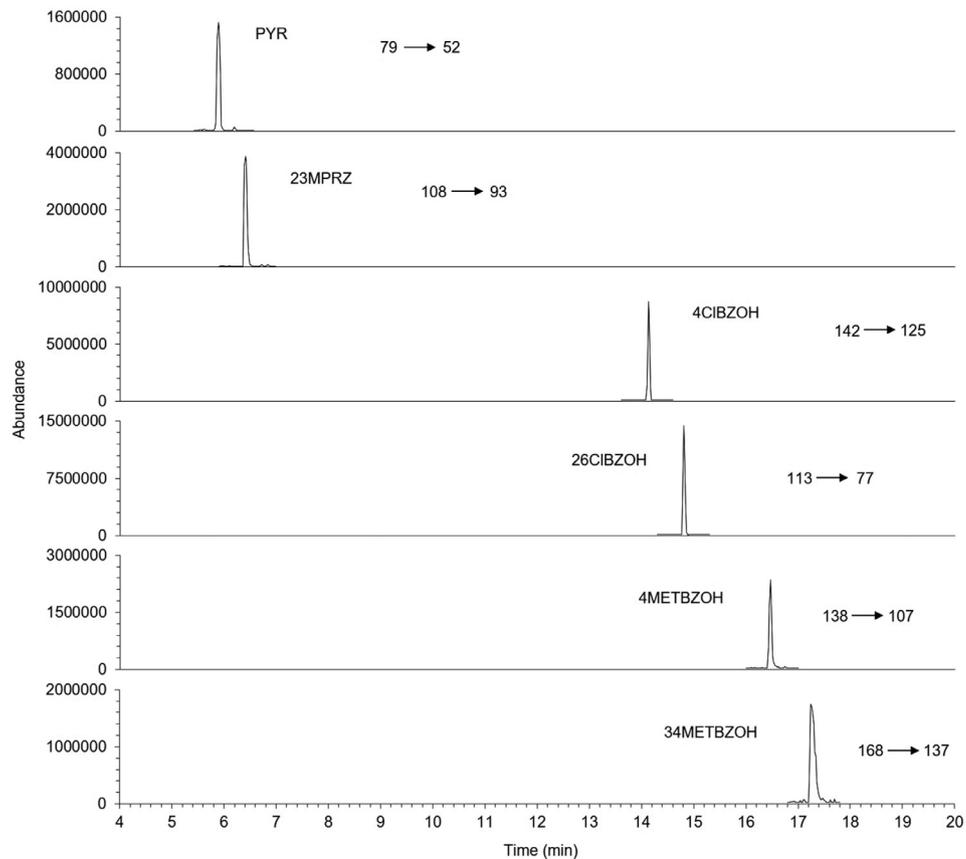**Fig. 3.** TIC of produced water from Ekofisk M spiked at 10 µg L^{-1} with all 6 target compounds

Fig. 4. Reconstructed SRM chromatogram of produced water from Ekofisk M spiked at 1 µg L^{-1} with all 6 target compounds.

Table 2
Linearity, limits of quantification and precision achieved with the developed method.

| Tracers | Linearity | | | Precision (% RSD) | | | | | |
| | | | | Intra-day precision | | | Inter-day precision | | |
	Range[a]	R^2	LoQ[a]	0.50[a]	2.5[a]	10[a]	0.50[a]	2.5[a]	10[a]
PYR	0.50 – 10	0.9995	0.35	7.9	6.6	6.2	9.4	7.4	7.3
23MPRZ	0.30 – 50	0.9970	0.20	4.7	5.3	4.2	7.1	7.2	5.3
4BZOH	0.10 – 20	0.9962	0.08	8.2	7.0	4.7	10	8,5	5.7
26BZOH	0.10 - 20	0.9971	0.10	6.2	7.1	4.2	8.1	7.8	5.6
4METBZOH	0.40 – 25	0.9974	0.25	9.4	7.4	5.9	12	9.1	5.4
26METBZOH	0.40 – 25	0.9984	0.25	10	6.4	3.9	12	11	7.5

[a] $\mu g\ L^{-1}$.

Table 3
Recoveries (%) and RSD (%) of the DI-HS-SPME-GC-MS/MS method in 8 real oilfield production waters spiked at 0.50 $\mu g\ L^{-1}$.

| Tracers | %Recovery (%RSD) – samples spiked at 0.50 $\mu g\ L^{-1}$ | | | | | | | |
	Snorre A	Snorre B	Ekofisk M	Gullfaks C	Heidrun A	Eldfisk A	Eldfisk S	Vigdis B
PYR	94.7 (7.8)	99.3 (8.1)	104 (5.7)	114 (6.6)	104 (8.7)	93.3 (7.9)	97.3 (6.4)	97.3 (8.3)
23MPRZ	105 (5.4)	98.7 (3.4)	95.3 (6.9)	94.0 (5.2)	97.3 (6.8)	95.3 (13)	103 (9.2)	108 (4.0)
4BZOH	97.3 (5.9)	90.0 (8.3)	86.7 (7.8)	101 (5.7)	96.7 (4.3)	101 (11)	99.3 (8.1)	100 (4.9)
26BZOH	101 (5.7)	91.3 (5.5)	103 (5.6)	93.3 (5.3)	98.0 (6.7)	96.7 (11)	97.3 (12)	101 (11)
4METBZOH	90.0 (4.8)	92.7 (9.0)	94.7 (6.1)	107 (6.9)	87.3 (4.7)	89.3 (6.4)	98.0 (9.3)	96.7 (5.2)
26METBZOH	88.7 (6.5)	86.7 (4.7)	90.7 (4.5)	101 (6.7)	99.3 (4.1)	88.7 (9.1)	93.3 (6.1)	94.7 (7.0)

Table 4
Recoveries (%) and RSD (%) of the DI-HS-SPME-GC-MS/MS method in 8 real oilfield production waters spiked at 2.5 $\mu g\ L^{-1}$.

| Tracers | %Recovery (%RSD) – samples spiked at 2.5 $\mu g\ L^{-1}$ | | | | | | | |
	Snorre A	Snorre B	Ekofisk M	Gullfaks C	Heidrun A	Eldfisk A	Eldfisk S	Vigdis B
PYR	96.0 (5.1)	98.9 (4.5)	107 (4.3)	98.8 (6.6)	104 (5.4)	108 (4.0)	97.9 (5.5)	96.5 (6.5)
23MPRZ	99.7 (6.4)	98.3 (5.2)	100 (4.1)	104 (9.2)	94.0 (7.0)	95.6 (4.8)	97.5 (6.3)	106 (4.8)
4BZOH	92.8 (3.4)	105 (7.4)	104 (4.3)	92.0 (6.1)	92.5 (6.0)	103 (3.7)	94.0 (6.5)	99.5 (6.8)
26BZOH	101 (5.4)	91.7 (5.8)	94.0 (2.8)	92.8 (7.4)	105 (7.3)	95.5 (8.4)	92.0 (6.9)	101 (7.1)
4METBZOH	103 (5.2)	95.2 (3.6)	93.6 (6.3)	97.3 (5.7)	91.3 (6.4)	95.9 (11)	102 (8.4)	96.1 (5.7)
26METBZOH	91.3 (6.3)	93.1 (4.0)	94.8 (6.9)	91.0 (8.2)	96.0 (6.2)	96.4 (4.7)	96,5 (3.7)	94.4 (6.4)

Mixed standard solutions were prepared in deionized water with concentrations starting at the calculated LOQ values and increasing, covering a wide range of values, to build calibration curves and evaluate the linearity of the method (the specific ranges for each compound are presented in Table 2). A direct linear proportional relationship was observed between the chromatographic response and the concentration of each of the analytes. Values for the coefficient of determination (R^2) were satisfactory and indicate good linear regression models for the chromatographic response vs concentration of each of the target compounds.

The precision of the full method was evaluated within a day (intra-day precision) and between 5 days (inter-day precision) at three different concentration levels (0.5, 2.5, and 10 µg/L). Results of the intra-day precision (n = 7) and inter-day precision (n = 5) are also summarized in Table 2.

The analytic method was used to screen for the 6 tracer compounds in production waters from 8 different Norwegian continental shelf oilfields (Snorre A, Snorre B, Ekofisk M, Gullfaks C, Heidrun A, Eldfisk A, Eldfisk S and Vigdis B). No signal of the presence of any of the analytes was detected in these samples. This is in agreement with one of the requirements for the technology: a tracer compound introduced into a given system, should be absent from it or present with a low and constant background so that the accuracy of the tracer test is not compromised. Of the 6 tracer compounds presented in the present manuscript only pyridine has been reported as a component of crude oils [41], however in relatively small amounts and mostly in the lighter hydrocarbon fractions. A PITT is primarily conceived for mature oilfields, thus the presence of pyridine (in significant amounts) is unlikely and

the results from the present study back this up. The other 5 compounds have never, to the best of our knowledge, been described as part of any oilfield fluid, and their industrial and household use makes their presence highly unlikely [3].

Recovery studies of the 6 tracer compounds were then performed on the 8 production water samples at three different concentration levels. Because none of the target compounds was detected in the original samples, no correction to calculate the recoveries was required. Different linear ranges were obtained for the different compounds and so the values for the concentrations of the spikes were selected in an attempt to represent low, medium and high values for all analytes. The three levels of concentration were as follows: 0.50, 2.50 and 10 µg L^{-1}, and the results for the recovery and %RSD are presented in Tables 3–5.

The results show a good performance of the method developed with all the recovery values between 85% - 115% and RSDs systematically ≤ 13%. The lowest systematic recoveries were observed for the methoxybenzyl alcohols. This is mostly likely due to their low volatility combined with the fact that the dominant period of SPME extraction is performed on HS mode relatively to the time of DI mode (15 vs 5 minutes). Of all the tested compounds, the measured responses for 4METBZOH and 34METBZOH showed the largest difference relatively to HS-SPME (see Fig. 2) after 30 minutes of extraction. Such suggests that, although 5 minutes of DI enhances the analytical system's response, this is not enough time for as fast equilibrium to be reached in the adsorption system (water → headspace → SPME fiber) for 4METBZOH and 34METBZOH, as this is not an exhaustive extraction technique. However, in summary, the results show that the method is suitable for analysis of

Table 5
Recoveries (%) and RSD (%) of the DI-HS-SPME-GC-MS/MS method in 8 real oilfield production waters spiked at 10 µg L^{-1}.

Tracers	%Recovery (%RSD) – samples spiked at 10 µg L^{-1}							
	Snorre A	Snorre B	Ekofisk M	Gullfaks C	Heidrun A	Eldfisk A	Eldfisk S	Vigdis B
PYR	96.0 (4.5)	97.8 (4.6)	96.4 (3.9)	97.4 (4.1)	101 (4.0)	102 (4.1)	101 (2.7)	96.7 (4.5)
23MPRZ	95.6 (1.6)	99.3 (4.5)	98.8 (3.3)	97.5 (5.0)	97.6 (4.2)	102 (4.2)	103 (5.8)	95.8 (4.4)
4BZOH	102 (4.2)	102 (3.8)	101 (2.8)	95.2 (3.5)	94.3 (5.6)	97.0 (3.5)	95.8 (4.9)	95.9 (6.2)
26BZOH	97.8 (3.1)	102 (5.2)	97.9 (3.7)	98.9 (4.3)	97.6 (3.5)	102 (4.8)	96.6 (4.6)	96.1 (4.9)
4METBZOH	96.2 (3.9)	94.7 (5.7)	97.8 (3.2)	95.8 (4.7)	95.7 (4.9)	94.6 (4.8)	93.2 (3.8)	95.9 (5.7)
34METBZOH	95.8 (5.2)	92.2 (5.9)	95.5 (4.0)	98.9 (3.6)	96.0 (4.4)	90.7 (4.2)	93.7 (3.9)	95.7 (5.0)

the 6 tracers in the intend matrix with a high sample output capacity.

4. Conclusions

An easy to automate analytical method consisting of sequential DI-HS-SPME extraction coupled to gas-phase chromatography and tandem mass spectrometry (GC-MS/MS) was developed for the identification and quantification of 4-chlorobenzyl alcohol, 2,6-dichlorobenzyl alcohol, 4-methoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, pyridine, and 2,3-dimethylpyrazine in production waters from oilfields. These compounds are promising PITT tracer candidates and a real test based on their use implies the analyses of hundreds of samples during a tracer campaign.

A DI-SPME approach combined with the addition of NaCl produced the best results of extraction, however proved unsuitable for real samples due to matrix effects. Sequential DI-HS-SPME was adopted to overcome this drawback and temperature and time of extraction were optimized. The final SPME extraction procedure consists of 5 mL of sample at pH 9.0 with 1.8 g of NaCl, constant stirring, 5 minutes of DI-SPME followed by 15 minutes of HS-SPME at 70 °C using a DVB/CAR/PDMS (50/30 µm) fiber.

The linearity and precision of the method were validated for all 6 target analytes. Linear behavior was observed for a wide range of concentrations (medium-low ng L^{-1} to low µg L^{-1}) and the LOQs were calculated to be between 0.080 and 0.35 µg L^{-1}. The method's recovery was evaluated at 3 concentration levels (0.50, 2.5 and 10 µg L^{-1}) in 8 real production waters from Norwegian offshore oilfields. The obtained recovery values were systematically higher than 85% and RSDs lower than 13%.

The sequential DI-HS-SPME-GC-MS/MS method was used to screen the production waters in the present study for the presence of the 6 compounds of interest. None of these compounds was detected in any of the samples, fact in line with the requirements for their use as an oilfield tracer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Mario Silva: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization, Validation, Writing - review & editing. **Tor Bjørnstad:** Validation, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

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Supplementary materials

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