Oil-in-Water Monitoring Using Membrane Inlet Mass Spectrometry

Boris Brkić,* Neil France, and Stephen Taylor*

Department of Electrical Engineering and Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, United Kingdom

ABSTRACT: A membrane inlet mass spectrometry (MIMS) system has been used for detection and analysis of two types of North Sea crude oil. The system was installed on-field on the Flotta Oil Terminal (Orkney, UK). It consisted of a quadrupole mass spectrometer (QMS) connected to the capillary probe with a silicone-based membrane. The produced mass spectra and calibration plots from the MIMS instrument showed the capability to measure levels of individual hydrocarbons within crude oil in seawater. The generated mass spectra from the field tests also showed the ability to distinguish between different types of oil and to determine concentrations of toxic hydrocarbons in oil (e.g., benzene, toluene, and xylene (BTX)). The performance of the instrument at different temperatures of seawater and oil droplet sizes was also investigated. The results showed that the QMS-based MIMS system has a potential to complement existing oil-in-water (OiW) monitors by being able to detect different oil types and specific hydrocarbon concentrations with high accuracy, which are currently not supported in commercially available OiW monitors.
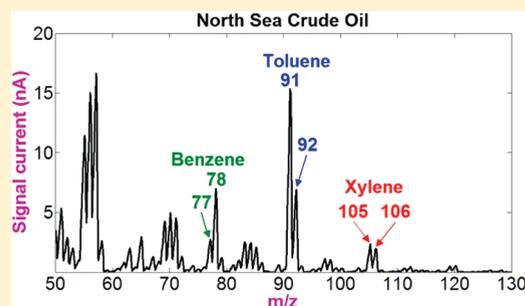
Oil-in-water (OiW) monitoring is a process of measuring concentrations of industrial oil and its substances in water.[1] Oil concentrations in the OiW industry are typically measured in parts per million (ppm). Types of oil that are most often monitored include crude oil, gasoline, diesel, jet fuel, and lubricating oils. The main industries that undertake OiW monitoring are the petroleum industry (oil platforms and refineries), petrochemical industry (petrochemical plants), power industry (power plants), and sewage industry (wastewater collection).[2,3] OiW monitoring in the petroleum industry is the main focus of this paper, which shows the potential of an alternative technique to complement techniques used in commercial OiW monitors on offshore oil platforms for controlling waste discharges.

OiW monitoring in the petroleum industry is achieved by controlling levels of crude oil in the produced water. This is the water that is produced together with oil from oil wells, extracted and piped to the surface. Using OiW monitors and suitable skimmers, oil levels in the produced water are controlled and oil is extracted from the water until the regulatory low level concentration limit is achieved. This limit is standardized by governmental agencies across the world. For example, in the UK, the oil discharge limit into the sea is 30 mg/L as specified by the Department of Energy and Climate Change (DECC).[4] Nevertheless, even with these limits, approximately 2.1 million barrels of oil per day worldwide are still discharged together with the produced water back into the sea.[5] This represents significant environmental and economic loss. Therefore, reliable and accurate analysis of crude oil and its components is essential to minimize this loss. To achieve this, the existing OiW monitors need to be improved and complemented with suitable analytical features.

Concentration of oil in water is measured using instruments that can detect concentrations of hydrocarbons in water, which are the main elements of industrial oils. Depending on OiW application, all three main classes of hydrocarbons (aliphatic, alicyclic, and aromatics) can be measured and analyzed. Several OiW monitoring techniques are being used on field, and they can be divided into two groups: (i) integral techniques that include gravimetry,[6] infrared (IR),[7] ultraviolet photometry (UVP),[8] and ultraviolet fluorescence (UVF),[9] and (ii) differential techniques that include gas chromatography mass spectrometry (GC-MS)[10] and liquid chromatography mass spectrometry (LC-MS).[11] Integral techniques are user-friendly, relatively fast for oil detection, and do not need sample preparation, but they cannot detect levels of individual substances contained in oils and distinguish between different oil types. On the other hand, differential techniques can determine detailed nature of the analytes with high reliability, but they require higher technical skills, longer detection times, and sample preparation.

To compensate for the disadvantages of differential techniques and maintain accurate analysis of oil analytes in water, a membrane inlet mass spectrometry (MIMS) can be used.[12−14] MIMS is an analytical technique for detecting trace organic compounds in air or aqueous solutions. In addition to being simple, accurate, fast for detection, and not requiring sample preparation, MIMS is highly sensitive, allowing low parts per trillion (ppt) detection levels for individual hydrocarbons.[15] It also has the capability to analyze a multicomponent species matrix simultaneously.[16]

With the development of miniature mass analyzers, such as quadrupole mass filters,[17−19] ion traps,[20−22] and time-of-flight analyzers,[23] portability of mass spectrometer systems used for MIMS has also been achieved,[24,25] which is important for field
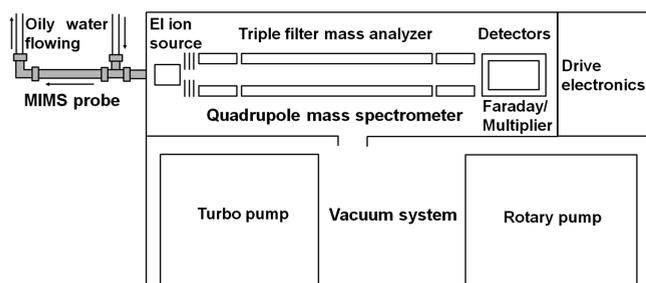
Figure 1. The schematic diagram for the MIMS system used for OiW monitoring on the North Sea Flotta Oil Terminal.

applications such as OiW monitoring. This is because smaller analyzers can operate at higher pressures, requiring less robust and less expensive vacuum systems that consume less power and allow battery operation. Also miniature analyzers can improve performance of the MIMS instruments by increasing mass range for a given voltage excitation[22] that enables hydrocarbons at higher masses to be detected.

The operating principle of MIMS is simple, and it is based on pervaporation separation,[26] usually enabled by a thin polymer-based membrane. A membrane is used as an interface between air or liquid that contains desired analytes and a vacuum system of a mass spectrometer. Using mechanism of pervaporation, the physical structure of a polymer membrane blocks water from passing through the membrane and allows other organic compounds to pass through the membrane. In this way, the analyte of interest dissolves into the membrane, diffuses through it, and evaporates into the vacuum system, where it first enters the ion source for ionization and then mass analyzer for spectral analysis. The generated mass spectrum helps to determine concentration levels of desired substances in a sample by observing the intensity of corresponding spectral peaks for each substance.

Previous work had shown the suitability of MIMS for rapid detection of hydrocarbons in water and the spectral analysis of major hydrocarbons in petrochemical compounds.[27] MIMS has also been applied for online wastewater monitoring at a wastewater purification plant at an oil refinery.[28] The latest results demonstrated the monitoring of crude oil at the subsurface of the sea during the Gulf of Mexico oil spill using a portable MIMS system on an autonomous underwater vehicle (AUV).[29] However, no monitoring of crude oil using MIMS has been reported during the control of waste discharges at oil drilling platforms.

This paper reports the first use of a portable MIMS system for field analysis of North Sea crude oil in water for the purpose of oil production process monitoring. The MIMS system consisted of a quadrupole mass spectrometer (QMS) connected to the sample probe with a capillary polydimethylsiloxane (PDMS) membrane. The field tests were performed for two types of North Sea crude oil with API 36 (type 1) and API 35 (type 2). The test results showed the capability of the MIMS instrument to distinguish between different oil types from the generated mass spectra and to determine levels of desired hydrocarbons. Effects of oil droplet size and water temperatures were also investigated, which is important for optimization of the instrument.

■ **EXPERIMENTAL SECTION**

Testing Environment and Experimental Field Setup. Field tests for OiW monitoring using the MIMS system were

performed at the Flotta Oil Terminal on Orkney Islands, which is the second largest oil terminal in the UK's part of the North Sea. The terminal is used for storing oil from many North Sea fields and distributing it within the UK and worldwide. It is currently operated by Talisman Energy.[30] The MIMS system was installed and tested on one of the terminal's oil plants owned by Opus Plus Ltd.,[31] which has facilities to simulate field conditions and to evaluate performance for various oil processing equipment. Figure 1 shows a schematic diagram of the MIMS experimental system built by the University of Liverpool for field tests. The three main components include the MIMS probe assembly, quadrupole mass spectrometer (QMS), and portable vacuum system housed in a metallic enclosure. Figure 2 shows the experimental setup for the Liverpool MIMS OiW monitoring system on the North Sea oil terminal. The monitoring results were recorded and analyzed on a laptop computer.

Sample Introduction. During field tests, the membrane sample probe was connected to the water system via 1/4 in. flexible rubber hoses. The water system had the pumping capability to provide 1–5 L/min flow rate of seawater at different temperatures, which is the flow rate range used on oil platforms worldwide. Oil was injected into the flow loop from the reservoir using a standard dosing pump with the ability to adjust oil concentration levels. Throughout the tests, the concentration of oil in seawater was determined by taking oily water samples and measuring the quantity of oil in mg/L using a Wilks Miran I variable filter infrared analyzer. To simulate field conditions, the oily water flow rate was kept at 3 L/min for all the tests with the water constantly flowing through the probe system and around the membrane (see Figure 1). The membrane that was used was capillary type, made from polydimethylsiloxane (PDMS) as described by Janfelt et al.[32] The PDMS capillary (Helix Medical Inc., Carpinteria, CA) was approximately 15 mm long with 0.28 mm wall thickness. Because of high water flow, the membrane was strengthened with a Hastelloy C rod with 2 μm porosity, which was positioned through the membrane. The porous rod was attached to the stainless steel sampling tube with 1/16 in. outer diameter and approximately 10 cm in length. The tube was connected to the inlet of a mass spectrometer to allow analyte molecules to enter the ion source for ionization.

Mass Spectral Analysis. Spectral analysis of ionized gas molecules passing through the membrane was performed using a quadrupole mass spectrometer (QMS) instrument supplied by Q-Technologies Ltd., a spin-out company from the University of Liverpool. The QMS consists of an electron impact (EI) ion source, a triple-filter quadrupole mass analyzer, and a dual detector. The EI ion source has dual Thoria filaments that provide 1.6 mA emission current. The separation between the source and the membrane during tests was approximately 15 cm. The mass analyzer has a m/z 1–200 mass range with unit resolution at 10% of the peak height for all spectral peaks. It contains a prefilter (25 mm long), main filter (125 mm long), and postfilter (25 mm long) with circular rods of 6.35 mm diameter. The analyzer is driven at 1.8 MHz rf drive frequency with autotuned voltages. Pre- and post filters are used for better ion focusing to improve sensitivity and have rf-only voltages applied. The main filter has suitable rf+dc voltages applied to perform mass scanning and enable resolution for mass peaks. The detector contains a Faraday cup for detecting the usual ion currents and a Channeltron-type electron multiplier for detecting very low currents such as those produced from hydrocarbons in low oil concentrations. The output from the detector (collector)

Figure 2. MIMS system field setup on the Flotta Oil Terminal.

Figure 3. Crude oil mass spectra for (a) type 1 (API 36) and (b) type 2 (API 35) North Sea crude with a 765 mg/L concentration obtained during field tests at the Flotta Oil Terminal using a portable MIMS system.

Figure 4. Crude oil lab mass spectra for (a) type 1 (API 36) and (b) type 2 (API 35) North Sea crude with 10 ppm concentration obtained at the University of Liverpool using a portable MIMS system.

varies between 1×10^{-5} and 1×10^{-4} Torr, depending on the temperature of the oily water.

■ RESULTS AND DISCUSSION

Oil-in-Water Detection and Analysis. The initial field tests at the Flotta Oil Terminal were performed to prove the principle for detection and analysis of crude oil in water using MIMS during the oil production process. Two types of North Sea crude oil with API 36 (type 1) and API 35 (type 2) were used for the experiments. Before testing crude samples in water, an air test and pure seawater test were performed as a starting reference point for the MIMS system. The oily water temperature during tests was 15 °C with 3 L/min flow rate. Figure 3a and 3b shows, respectively, the hydrocarbon mass spectra for types 1 and 2 of North Sea crude in water with a mass range m/z 50−130. The concentration for both types of oil was 765 mg/L, measured using an IR analyzer. Flotta crude has a density of 837 g/L at 20 °C,[33] where 1 ppm = 0.837 mg/L.

Figure 3 shows that the major hydrocarbons for both crude types are detected including toxic aromatic hydrocarbons benzene, toluene, and xylene (BTX). They are represented through their typical fragment ions m/z 77 and 78 (benzene), m/z 91 and 92 (toluene), and m/z 105 and 106 (xylene). Note that traces of xylenes could also be present at m/z 91 and 92 as well as small traces of other hydrocarbons that naturally occur in crude oil such as cyclohexane and naphthalene at m/z 77 and 78. This enables the determination of concentration levels for major toxic analytes in oil using the intensity of their spectral peaks. It can also be seen that hydrocarbon spectral peaks for type 2 crude have significantly lower intensity than type 1 crude peaks, especially BTX peaks for the same oil concentration. This is due to the nature of type 2 crude because it contains more sand and reservoir solids, which reduce the strength of the output signal. Therefore, different oil types generate different mass spectra, which helps to determine oil types contained in

is connected to the drive electronics for data acquisition. During spectral analysis, 10 acquisition points were recorded per unit mass with an average number of 100 scans per test throughout the whole mass range.

Vacuum System. The whole QMS system consists of a QMS and high vacuum system to allow QMS operation. Vacuum system, provided by Q-Technologies Ltd., consists of a vacuum chamber, an Edwards 1.5 rotary pump, and a Pfeiffer Balzers TPH 062 turbomolecular pump. The rotary pump is used as a backing pump for the turbomolecular pump, providing a pressure down to 1×10^{-3} Torr, while the turbomolecular pump gives a base pressure of 1×10^{-6} Torr. With a membrane probe attached to the QMS system, the operating pressure usually

Figure 5. Calibration curves for benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105) for type 1 (a−c) and type 2 (d−f) North Sea crude oil obtained during field tests at the Flotta Oil Terminal using a portable MIMS system.

produced water on the oil rigs and supplement functionality of the existing OiW monitors.

Because of limitations of the oil injection apparatus at the Flotta, fine adjustment of oil concentrations was not possible and the lowest measured on-field concentration was 15 mg/L for type 2 crude. A 10 ppm concentration for both North Sea crude types was measured in the University of Liverpool lab with the corresponding hydrocarbon mass spectra shown in Figure 4 for a m/z 50−130 mass range. Water within the lab flow system was at room temperature (25 °C) with 1.8 L/min flow rate where the oil concentration was adjusted in ppm using a precision syringe. A detected concentration of BTX was less than 100 ppb because it is usually less than 1% of the total amount of oil.[29] The existing capillary membrane could possibly detect even lower oil concentrations (down to 1 ppm). If detection of hydrocarbons at low ppb levels is required, a significantly thinner membrane can be used together with carrier gas for analyte enrichment.[34] Low ppt levels can be achieved by further enrichment of carrier gas using a jet separator that allows two-stage analyte enrichment.[35]

Oil Concentration Tests. Like commercial OiW analyzers, a MIMS instrument can also be used for measuring crude oil concentrations in water. To achieve the most reliable concentration measurement, a suitable m/z should be chosen that has a calibration curve with the highest linearity. This will enable specification of a corresponding signal current range for each oil concentration under different conditions (e.g., water temperatures). It was found during tests that ions corresponding to BTX molecules exhibit higher linearity in signal intensity with concentration than that of other hydrocarbons in North Sea crude mass spectra. A possible reason for this may be the mechanical properties of the PDMS material. Because of the elastomeric nature of PDMS, absorbed hydrocarbons can cause swelling in the membrane material by making changes in the cross-sectional area of micropores, which will affect the analyte flow rate.[36] Previous work by LaPack et al.[37] has already demonstrated different experimental values for permeation parameters for aromatics and alkanes in a silicone-based membrane at room

temperature (25 °C). The physical structures of individual hydrocarbon molecules in crude oil may also affect permeability through PDMS. For example, the hexagonal ring structure of benzene and its derivatives may allow a higher permeation rate through the pores of the membrane and porous rod compared to other hydrocarbons in crude oil that have more complicated 3D structures and may have more difficulty to pass through membrane pores at higher concentrations. Other possible reasons for different permeability rates at different concentrations include the mechanical properties of the porous rod, sample temperature, and physical interactions between individual hydrocarbons in crude oil, which will be the subject of future research.

Figure 5 shows the calibration curves for benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105) for type 1 (Figure 5a−c) and type 2 (Figure 5d−f) North Sea crude oil, obtained with the MIMS system during field tests. These m/z values were chosen because they give slightly higher linearity than m/z 77, 92, and 106. Seven concentration tests were performed for each oil type, and they were measured using an IR analyzer. Concentrations for type 1 crude were 34, 94, 135, 305, 559, 765, and 853 mg/L, while concentrations for type 2 crude were 15, 124, 295, 341, 500, 765, and 892 mg/L. Because 1 ppm = 0.837 mg/L for the Flotta crude, the concentration range for the tests was up to approximately 1000 ppm for both crude types. As can be seen from concentration points on the plots, calibration curves with the highest linearity are for benzene in both crude types. Values for the linear regression coefficient R^2 are shown on each plot in Figure 5. R^2 values for benzene are 0.9488 and 0.9102, respectively, for crude types 1 and 2, which is within an acceptable level for determining oil concentration. The calibration curves for toluene and xylene show more saturation at higher concentrations (above 500 mg/L), and it will be more difficult to obtain their levels in this range. The higher the oil concentration, the more saturation will occur in the intensity of spectral peaks after reaching the solubility limit. This prevents injection of analytes, which reduces linearity.
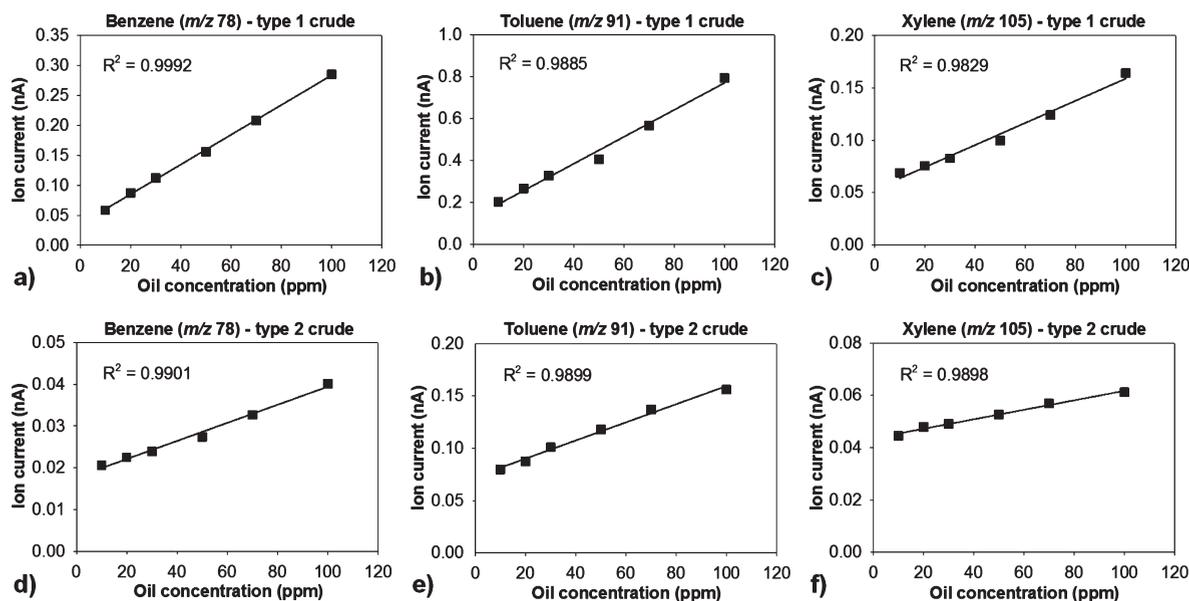
Figure 6. Calibration curves for benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105) for type 1 (a−c) and type 2 (d−f) North Sea crude oil obtained at the University of Liverpool using a portable MIMS system.
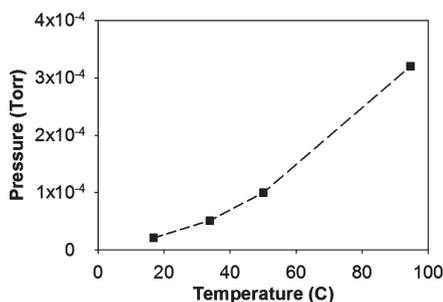
Figure 7. Variation of the MIMS system operational pressure with an oily water temperature for type 1 North Sea crude oil during field tests at the Flotta Oil Terminal using a portable MIMS system.

A high linearity for the BTX calibration curves and more reliable level detection can be achieved at lower oil concentrations. Figure 6 shows the lab-obtained calibration curves for benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105) for type 1 (Figure 6a−c) and type 2 (Figure 6d−f) North Sea crude oil for a concentration range between 10 and 100 ppm at room temperature. As can be seen, linearity has been greatly improved, giving high R^2 values for all BTX components. This enables reliable detection of BTX and crude levels at lower oil concentrations, which is the range commonly used on oil platforms.

Oily Water Temperature Tests. The purpose of doing temperature tests was to investigate effects of oily water temperatures on the operational pressure of the MIMS system and PDMS membrane. Water temperatures above 100 °C can cause signals to fall to almost zero level and cause damages to silicone membranes.[16] Typical produced water temperatures on oil platforms vary between 30 °C and 70 °C, being a safe range for silicone membranes, although in very specific cases produced water temperatures could be as high as 120 °C.[38]

Figure 7 shows changes of partial pressure with an increase in temperatures of oily water with 108 mg/L oil concentration. Temperatures that were used for the tests were 16.8 °C, 33.8 °C, 50.1 °C, and 94.6 °C. Water flow rate was 3 L/min. The plot in

Figure 7 shows that the increase in seawater temperature from 16.8 °C to 94.6 °C caused a 15 fold increase in partial pressure from 2.1×10^{-5} to 3.2×10^{-4} Torr. This is important to be known for safe operation of ion sources because most hot filament EI ion sources can operate safely up to 1×10^{-4} Torr with the exception of glow discharge (GD) EI sources that can operate at significantly higher pressures.[39] After 1 h at 94.6 °C, there was no visible damage to the MIMS membrane, which shows good heat resistance by the PDMS material. Therefore, it can be concluded that safe operation of a MIMS system is achievable for a typical produced water temperature range of 30−70 °C.

Operation of the MIMS instrument at higher sample temperatures will cause expansion of micropores on the membrane, which allows higher analyte flow into the vacuum system and increased partial pressure. It is already known that temperature directly affects diffusion and solubility of the membrane as well as partial pressure.[14] During field tests, higher sample temperatures increased intensity for all spectral peaks because of improved diffusion of the membrane through expansion, which has also been reported by LaPack et al.[40]

Oil Droplet Size Tests. Variation of oil droplet size has been performed in order to investigate whether different droplet sizes affect intensities of spectral peaks for a given oil concentration. Table 1 shows field test results with variation of signal intensity for BTX with droplet sizes of 8.9, 14, 30, and 39 μm at initial 100 mg/L concentration of type 1 North Sea crude. Like oil concentration, oil droplet size was also measured using a Wilks Miran I variable filter infrared analyzer. Sea water temperature was 15 °C with 3 L/min flow rate. Table 1 shows very small changes in BTX signal strength for different droplet sizes. Even these changes may not be influenced by the droplet size change, but caused by shear valve adjustment for controlling droplet size, which may have altered oil concentration.[41] Therefore, different oil droplet sizes for the given oil concentration most likely do not have any effect on mass spectra, meaning that their influence can be excluded from the calibration procedure of the MIMS instrument.

Table 1. BTX Signal Intensity Variation for Different Droplet Sizes of Type 1 North Sea Crude at 100 mg/L Concentration Obtained during Field Tests at the Flotta Oil Terminal a Using Portable MIMS System

oil droplet size (μm)	benzene (m/z 78) signal intensity (nA)	toluene (m/z 91) signal intensity (nA)	xylene (m/z 105) signal intensity (nA)
8.9	1.19	4.91	1.43
14	1.22	5.04	1.50
30	1.25	5.01	1.41
39	1.18	4.95	1.37

Instrument Response Times. When calculating response times for polymer membranes, usually 50% response time is taken. This is because asymptotic behavior of the pervaporation process makes steady-state time (90% or higher) of the analyte difficult to be determined. The 50% response time $t_{50\%}$ is given by:[40]

$$t_{50\%} = 0.14(L^2/D) \tag{1}$$

where L is the thickness of the membrane and D is the diffusion coefficient of the analyte in the membrane. Transfer of the analyte through the membrane is described using steady-state flow rate I_{ss} given by:[13]

$$I_{SS} = ADS(P_S/L) \tag{2}$$

where A is the membrane surface area, S is the solubility constant, and P_s is the partial pressure of the analyte.

During field tests with the MIMS instrument, average 50% response times for benzene (m/z 78), toluene (m/z 91), and xylene (m/z 105) were, respectively, 2, 4, and 7 min with a 0.28 mm thick capillary membrane. If needed, response of the instrument can be significantly faster by using a thinner membrane (see eq 1), which will also increase the sensitivity of the instrument (see eq 2). It was already proven experimentally that very fast response times can be achieved using extremely thin membranes close-coupled to the ion source.[42] At the moment there is no specified requirement for the length of response time of the MIMS system for OiW monitoring. UVF analyzers, the most widely used OiW monitors, produce a scanning result for oil concentrations every 10 min.[43] If the MIMS system is to be used as support for commercial OiW monitors with the ability to monitor different oil types and their components, then data generation even within 30 min should be acceptable.

Instrument Calibration. After the proof of principle, in order to produce reliable data, calibration of the MIMS instrument is required. This is because permeability of PDMS membranes that affects signal intensity is highly dependent on external factors such as water temperature, hydrostatic pressure, and hydrodynamics (water flow rate). Influence of hydrodynamics may be avoided by placing a membrane probe into an oily water sample without a flow and doing ultrasonic cleaning of the membrane after each OiW analysis, instead of using the flushing method. It was found during lab tests that mass spectra can be obtained without water flow with the existing membrane for relatively low crude concentrations (e.g., 50 ppm) with water temperatures above 40 °C, at the expense of losing sensitivity.

Calibration of the instrument at different temperatures is an important factor. It can be performed for the required temperature range (30 °C to 70 °C) and lower oil concentrations (up to 100 ppm), where the linear increase in BTX signal intensity is expected with temperature increase. This will help to determine the concentration of oil and the desired analyte from the intensity of selected spectral peaks at a specific water temperature. Influence of hydrostatic pressure can also be added to the calibration procedure by using correction methods proposed by Bell et al.[44] in which output data was successfully calibrated.

■ CONCLUSIONS

This paper has demonstrated the proof of principle for on-field detection of crude oil using a portable membrane inlet mass spectrometer that performed analysis for two types of North Sea crude oil. Oil concentration tests were conducted in order to produce calibration curves that can help to determine the concentration of oil and its substances at higher and lower concentrations. Oily water temperature tests were performed to test heat resistance of the PDMS membrane and temperature effects on the operating pressure of the MIMS system. Oil droplet size tests showed that the droplet size for a given oil concentration does not cause any significant change in signal intensity. Response times for benzene, toluene, and xylene were reported with suggestions for further improvement if necessary.

Future work will include further calibration and optimization of the existing MIMS system. Instrument development to include a thinner membrane will be used to provide higher sensitivity and faster response times. Usage of atmospheric pressure ion sources will be considered to allow safe operation of a MIMS system at higher pressures that occur at high oily water temperatures. A mass analyzer with higher mass range (e.g., ion trap) could also be used to detect high mass hydrocarbons in crude oil spectra. A final stage will involve coupling of the MIMS instrument to one of the existing commercial OiW monitors and its usage at oil platforms.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: Boris.Brkic@liv.ac.uk (B.B.); S.Taylor@liv.ac.uk (S.T.).

■ ACKNOWLEDGMENT

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