

## ***Introduction***

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Accurate measurement of dispersed oil-in-water (OIW) has become increasingly more important as International regulations are implemented, including the 2000/2001 Oslo/Paris Convention (OSPAR) and ISO 9377-2, the UK Dispersed Oil in Produced Water Trading Scheme, and the Norwegian State Pollution Control Authority (SFT). Each of these regulations now requires off-shore oil platforms monitor their discharge into the sea. OSPAR also recommends that no individual off-shore installation should exceed a set performance standard for dispersed oil of 30 mg/L for produced water discharged into the sea. Oil refineries in the designated regions are also beginning to comply to both the OSPAR method and ISO 9377-2.

With the implementation of these regulations, it is imperative that off-shore platforms and refineries comply with these rules, and demonstrate to regulators and government bodies that effective and accurate oil-in-water monitoring is taking place, as non-conformance of these regulations can result in financial penalties. In addition to the benefits to the environment, with opportunities to participate in emission trading schemes, the reduction of OIW also benefits the oil operations themselves, as elevated OIW concentrations can potentially plug disposal wells, lines, pumps and valves with suspended oil droplets.

OSPAR now recommends using gas chromatography and flame ionization detection (GC-FID), as described in the modified ISO 9377-2 GC-FID. Although the legal requirement to use this method has not yet been implemented widely, Norway has chosen to adopt this method. Since chlorinated solvents can no longer be used, this removes the option of using infrared (IR) analysis to measure the OIW. The implementation of these new methods has many oil refineries research the impact of bringing both sample preparation and testing on-site, as outsourcing can be expensive.

Related documentation has discussed some of the difficulties faced in regards to the OIW monitoring process. This can potentially create confusion as to what is required to be measured when the new implementations take place. For example; many methods require chemicals such as biocides, emulsion breakers, and corrosion inhibitors be used during Liquid-Liquid Extractions (LLE). The efficient and accurate use of these chemicals is reliant on factors including information such as the amount of oil in the water, and droplet size of the oil, but these factors are often unknown.

The use of Solid Phase Extraction (SPE) eliminates many of the problems that can occur during the extraction step. SPE involves passing the liquid sample through a solid phase disk. This eliminates the problem with emulsions, and therefore the use of chemicals that would be required to remove these emulsions. SPE can also be automated, and performed in a single extraction step, reducing the time and labor associated with LLE. Horizon Technology's SPE-DEX® 4790 Automated Extraction System provides many benefits when compared to LLE. The use of an automated system decreases solvent usage; the amount of operator time involved, and improves the accuracy and consistency of results.

Data collected at StatoilHydro Mongstad, in Norway which had a 2-place Horizon Technology SPE-DEX® 4790 Automated Extractor System, provided evidence to strongly support the use of automated SPE. Prior to the installation of the SPE-DEX® 4790 Automated Extractors, manual LLE was the method being used, resulting in emulsions, longer time taken to perform the extractions, and imprecise sample recoveries.

With the installation of the SPE-DEX® 4790 Automated Extractor System excellent recoveries were immediately recognized due to the automation and reverse phase interactions between the OIW compounds (C10 to C40) and the Horizon Technology Atlantic® DVB SPE disks that were used. Once the OIW compounds were captured onto the disk, solvents were selected to elute these compounds, such as Hexane or Pentane. These solvents interrupt the absorption that occurs between the SPE disk and OIW compounds, allowing for proper elution of the compounds

## ***Instrumentation***

- Horizon Technology SPE-DEX® 4790 Automated Extractor System
- Horizon Technology Atlantic® DVB Disk
- 125 mL separatory collection vessel
- Thermo Electron's TRACE GC with the Ultra Fast Module (UFM) and Programmable Temperature Vaporizing inlet / FID configuration
- Thermo Electron's TriPlus Autosampler

## ***Method Summary***

- 1) Approximately 1000 mL water samples were used and weighed to calculate actual volume.
- 2) Spike the samples with 4.0015 mg of BAM K0009 ref oil (Ref: Absolute Standards Part # 95200).
- 3) Adjust the water sample to a pH = 2.0
- 4) Place the sample bottle on the SPE-DEX® 4790 Automated Extractor and the Atlantic® DVB SPE Disk in the disk holder.
- 5) Place the sample collection vial on the extractor with 1 mL of DI water in it.
- 6) After approximately 25 minutes collect the final elution.
- 7) Pour off the lower Methanol/Water layer.
- 8) Measure the amount of Pentane in the final collection.
- 9) Analyze by GC/FID

## ***Results***

All water samples were processed using the following method, developed in the laboratory at Horizon Technology.

After the spiked samples were prepared, the collection vessel was placed on the extractor. Prior to placing the vessel on the extractor, 1.0 mL of DI water was placed in the sample collection vessel to help draw out any trace water from the Pentane phase, and into the Methanol phase during sample elution. The Atlantic® DVB SPE Disk was then placed in the disk holder and the sample loaded onto the extractor, and the method started. After the pre-wets had finished cleaning, activating and wetting the disk, the sample was processed and analytes concentrated onto the disk. The first Methanol rinse was used to remove any trace water that remained on the disk so that the Pentane could fully interact with the OIW analytes. Pentane was then introduced to the disk four times,

**Table 1: SPE-DEX® 4790 Extraction Method**

STEP	SOLVENT	SOAK TIME	DRY TIME
Prewet #1	Pentane	1:00 Min	0:30 s
Prewet #2	Methanol	1:00 Min	0:30 s
Prewet #3	Reagent Water	1:00 Min	0:30 s
Prewet #4	Reagent Water	0:00 s	0:00 s
Sample Process			
Air Dry			0:30 s
Rinse Step #1	Methanol	3:00 Min	0:20 s
Rinse Step #2	Pentane	3:00 Min	0:20 s
Rinse Step #3	Pentane	2:00 Min	0:20 s
Rinse Step #4	Pentane	2:00 Min	0:20 s
Rinse Step #5	Pentane	2:00 Min	1:00 Min

with long soak times, to ensure thorough interaction with the analytes.

Once the method completed minimal handling was required. After gently mixing the phases by hand, the lower Methanol/water layer was poured off of the bottom of the 125 mL separatory funnel and discarded. Since the OSPAR method does not allow concentration, the Pentane phase was poured into a pre-weighed VOA vial, the Pentane weight was measured, and the volume calculated. (Note: It is common for Pentane volumes to vary from sample to sample due to the volatility of the solvent.) Once the volume was known, the samples were spiked with C<sub>10</sub> and C<sub>40</sub> to enable the limits of measurement to be easily identified. These peaks can be seen in Figure 1 on the following page.

## ***Validation study***

A validation study was conducted at StatoilHydro Mongstad, which focused on selectivity, accuracy, precision (repeatability and intermediate precision), limits of detection, limits of quantification, as well as linearity.

Linearity was tested from blank water samples spiked with OIW standard concentration ranges of: 0.2 mg/L, 0.6 mg/L, 1.0 mg/L 5.0 mg/L and 10 mg/L. Selectivity was demonstrated by the analysis of blank samples compared with blank samples spiked with oils. Repeatability was evaluated by two replicated injections of three repeated analysis (n=3) of water samples spiked in 5 concentration levels during 1 day. Intermediate precision was determined by two replicate injections of two repeated analysis in 3

concentration levels during 5 days. Each sample in each group was tested at least one week apart with at least three other samples between. Accuracy was determined by finding recovery in samples from intermediate precision. Limits of detection and limits of quantification were estimated by analyzing 20 blank samples. The LOD and LOQ were calculated as 3 and 10 times of the signal from the blank samples, respectively

The results, shown in Figures 2, 3 and 4, on the following page show no signs of interference peaks from blank samples which were extracted by the SPE-DEX® 4790 Automated Extractor. The method shows excellent selectivity. RSD values for repeatability varied between 3.9% and 11.2% and for intermediate precision between 5.3% and 10.5% at different concentration levels. Accuracy is determined to be from 80%-115%. LOD and LOQ were determined to be 0.2 mg/l and 0.6 mg/l, respectively. The method showed a linear response over a range of concentration, 0.2-10 mg/l ( $r=0.997$ ).

### Conclusions

The practice of OIW measurement under the OSPAR method calls for accurate, reproducible measurements using a GC/FID. In this study coupling the Horizon Technology SPE-DEX® 4790 Automated Extractor System, and the Horizon Technology Atlantic® DVB SPE Disk, proved to be a better alternative to traditional LLE methods. The SPE-DEX® 4790 Automated Extractor System eliminated emulsions, had proven higher recoveries, and was reproducible.

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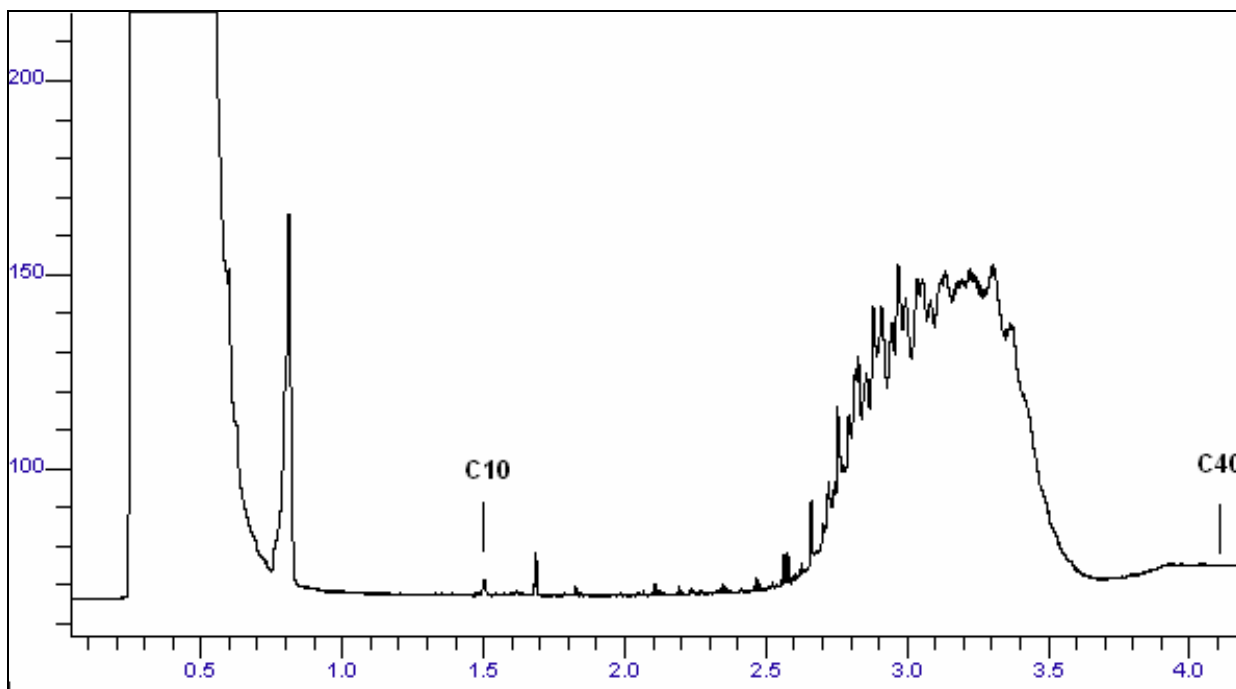


Figure 1: OIW Sample Chromatogram



## Determination of Dispersed Oil in Water Using Automated SPE in Compliance with OSPAR and ISO 9377-2 Methods in Norway

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Spike	Analyser 1		Analyser 2		Analyser 1		Analyser 2		Analyser 3		Intermediate precision	
	Day 1		Day 2		Day 3		Day 4		Day 5		SD	RSD %
	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %		
0.6 mg/L	0.76	126.7	0.61	101.7	0.56	93.3	0.60	100.0	0.52	86.7	0.06	10.5
	0.68	113.3	0.62	103.3	0.60	100.0	0.66	110.0	0.50	83.3		
	0.68	113.3	0.55	91.7	0.58	96.7	0.59	98.3	0.51	85.0		
	0.66	110.0	0.61	101.7	0.59	98.3	0.65	108.3	0.59	98.3		
SD	0.04		0.03		0.02		0.04		0.04			
RSD% Repeat ability	6.4		5.4		2.9		5.6		7.7			

Figure 2: Validation data for 0.6 mg/L samples

Spike	Analyser 1		Analyser 2		Analyser 1		Analyser 2		Analyser 3		Intermediate precision	
	Day 1		Day 2		Day 3		Day 4		Day 5		SD	RSD %
	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %		
5.0 mg/L	5.2	104.0	5.2	104.0	4.8	96.0	4.5	90.0	4.4	88.0	0.48	10.1
	5.5	110.0	5.1	102.0	4.6	92.0	4.0	80.0	4.2	84.0		
	5.2	104.0	*	*	4.5	90.0	4.7	94.0	4.4	88.0		
	5.7	114.0	*	*	4.7	94.0	4.4	88.0	4.2	84.0		
SD	0.24		0.07		0.13		0.21		0.12			
RSD% Repeat ability	4.5		1.4		2.8		4.8		2.7			

Figure 3: Validation data for 5.0 mg/L samples



## Determination of Dispersed Oil in Water Using Automated SPE in Compliance with OSPAR and ISO 9377-2 Methods in Norway

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Spike	Analyser 1		Analyser 2		Analyser 1		Analyser 2		Analyser 3		Intermediate precision	
	Day 1		Day 2		Day 3		Day 4		Day 5		SD	RSD %
	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %	mg/L	Accuracy %		
<b>10.0 mg/L</b>	10.1	101.0	9.9	99.0	9.1	91.0	9.4	94.0	9.5	95.0	0.52	5.34
	10.7	107.0	10.7	107.0	9.1	91.0	9.4	94.0	9.4	94.0		
	9.8	98.0	*	*	10.0	100.0	9.1	91.0	9.4	94.0		
	10.2	102.0	*	*	9.6	96.0	9.3	93.0	9.1	91.0		
<b>SD</b>	0.37		0.57		0.44		0.14		0.17			
<b>RSD% Repeat ability</b>	3.7		5.5		4.6		1.5		1.8			

Figure 4: Validation data for 10.0 mg/L samples