ECOLOGICAL AND ECONOMICAL MEASUREMENT OF OIL-IN-WATER WITHOUT COMPROMISING ACCURACY

The measurement of hydrocarbons in water is a routine task in basically every chemical complex that somehow discharges water into a municipal sewage system or into any type of surface water body. Routine analysis in general should be easy to carry out and cost-effective in terms of initial and running costs. If it comes to environmentally relevant parameters such as oil-in-water concentrations in discharge water governmental bodies play another important role. They usually regulate the maximum concentrations that can be discharged and penalize offenders of these limits. Highly accurate and precise analyzers are needed to mitigate the risk of exceeding admissible values and getting fined. Classical InfraRed (IR) spectroscopy offers both, high accuracy and excellent repeatability. However, to take full advantage ecologically harmful solvents such as CFCs have to be used. In this paper we discuss results from our latest development that combines all benefits of IR spectroscopy with the safe, CFC-free solvent cyclohexane.

Oil-in-water measurement techniques – an overview

Prior to the ban of CFC solvents by the Montreal Protocol oil-in-water measurements were conducted by a liquid-liquid extraction of the aqueous sample with a CFC solvent followed by an infrared spectroscopic measurement according to ASTM D3921 or DIN 38409-H18. These fluorinated and chlorinated solvents, regrettably, harm the earth's ozone layer and most of them are forbidden by now. This ban and the continuing demand for the measurement of oil-in-water content led to the development of new measurement techniques.

In the US a gravimetrical method was adopted where the aqueous sample is extracted with hexane. This extract is then dried on a heated balance until all solvent is evaporated. The residue is then weighed. The most commonly applied standard is EPA 1664 B which defines two parameters: HEM – n-Hexane Extractable Material and SGT – Silica Gel Treated n-Hexane Extractable Material. HEM contains every substance that can be extracted with n-hexane which includes hydrocarbons, grease, animal fat and vegetable oil. However, usually only the hydrocarbon part is interesting to legal bodies. Therefore, the parameter SGT is measured after treating the extract with silica gel which retains polar substances such as vegetable oil.

In Europe the shift away from the infrared spectroscopic methods led towards gas chromatography. The current standard in Europe is ISO-9377 which uses a solvent or solvent mixture with a boiling range between 36°C and 69°C for the extraction of the aqueous sample. After the extraction the sample is cleaned up by filtrating it through a glass column filled with 2g of Florisil and 2g of sodium sulfate. During this clean-up step all polar substances are removed analogous to EPA 1664. The final extract is then measured using a gas chromatograph. From the chromatogram the so-called hydrocarbon index is calculated which takes only molecules between 10 and 40 carbon atoms into account. Lighter or heavier molecules are not considered as hydrocarbons by this method.

From the aforementioned it is very clear that both methods deliberately exclude parts of the hydrocarbon range due to evaporation loses or because they are not taken into account during the calculations. In both cases limitations of the measurement methodology itself lead to these measurement errors. It also shows how difficult it is to compare results from one method to the other as substances measured by the first method may be excluded by another.

With ASTM D7066 and ASTM D7678 two infrared methods are available. ASTM D7066 uses the CFC solvent 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane (S-316) or complex mixture of CFCs known as H-997. For both substances the phase out period will end January 2020 [1]. ASTM D7678 on the other hand uses the environmentally friendly solvent cyclohexane. It defines the parameter total petroleum hydrocarbon (TPH) as every substance that can be extracted with cyclohexane which is then filtrated over Florisil to remove any polar substances. The measurement principle, however, differs from previous IR methods which all measured the spectral region of the CH stretching vibrations as can be seen in figure 1. ASTM D7678, in comparison, measures the CH_3 deformation vibration which isn't present in the IR spectrum of cyclohexane due to the lack of a CH_3 group.

ASTM D7678 would be the ideal measurement method for oil-

ERACHECK ECO –
simple, economical and ecological sub-ppm oil-in-water measurements

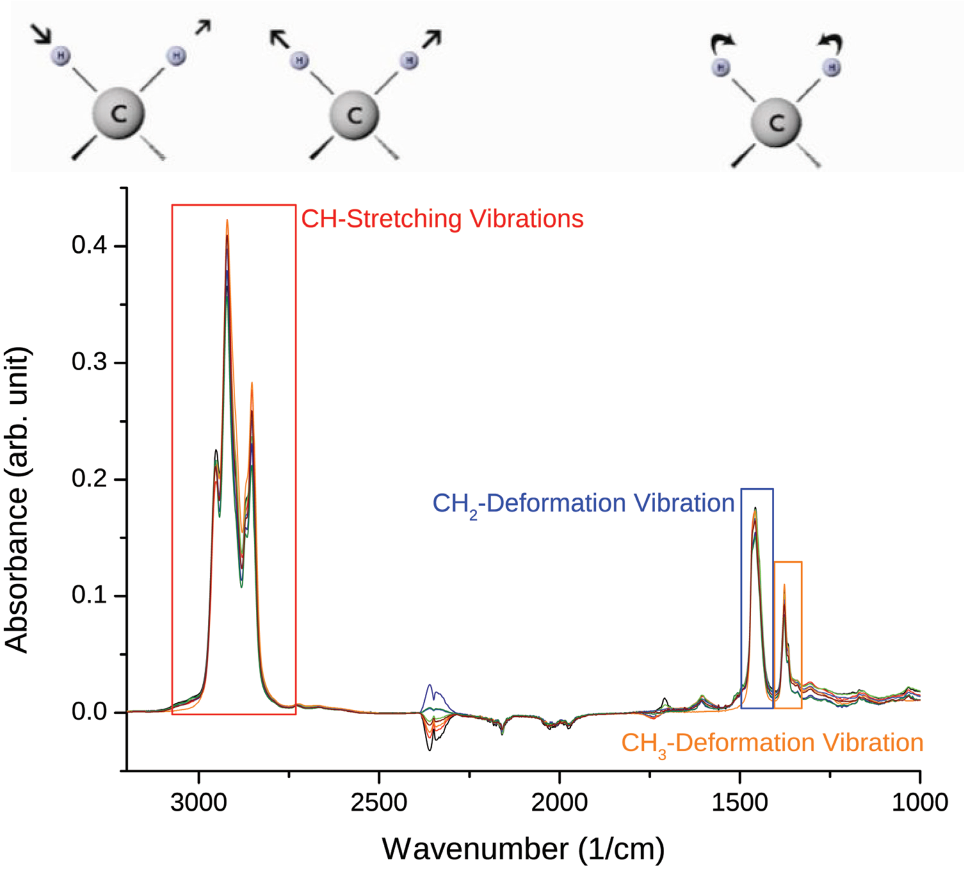

Figure 1: Absorbance spectra of crude oil samples from different sites in the North Sea. The more prominent signal of the C-H deformation region is caused by CH_2 groups whereas the smaller band to the right originates from CH_3 groups. Cyclohexane lacks CH_3 groups and therefore only exhibits the CH_2 signal.

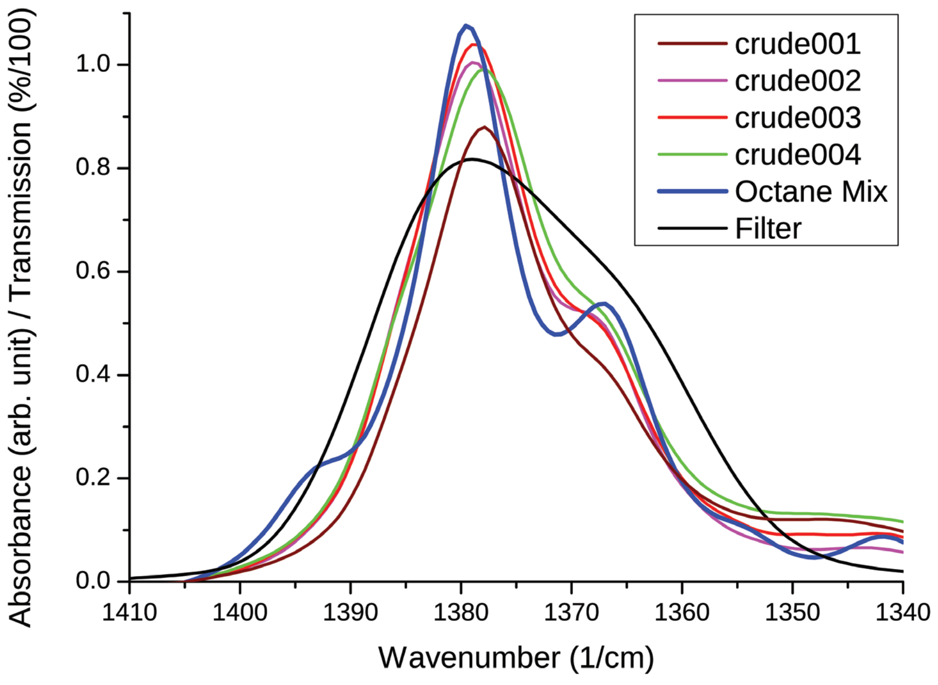

Figure 2: Absorption spectrum in the CH$_3$ deformation vibration region of four different, the octane / iso-octane calibration mixture overlaid with the transmission characteristic of the optical filter.

in-water – it is fast, easy and uses an environmentally friendly extraction solvent. Unfortunately the cost of the Quantum Cascade Laser (QCL) used in eralytics' analyzer ERACHECK PRO, covering ASTM D7678, is high and therefore many routine labs didn't adapt to this method.

Since the release of the ERACHECK PRO in 2008 eralytics' R&D team further improved on the measurement technology using cyclohexane for the extraction. All these efforts culminated in a new instrument called ERACHECK ECO because of its economical and ecological design. This paper summarizes its performance and elaborates on the applied measurement technique.

Measurement Principle

This new oil-in-water tester ERACHECK ECO is based on an old but reliable measurement principle: non-dispersive IR spectroscopy. In such systems a light source emits light predominantly in the infrared region of the spectrum. An optical element transmits light only in the spectral region of interest and blocks all other wavelengths. The transmitted part of the light then travels through the sample cuvette where it is attenuated due to absorption by the sample's molecules. The remaining light is measured by a detector. To gain analytical information it is necessary to measure only the amount of light that is actually absorbed by the sample itself. Therefore two measurements are performed. First the sample cuvette with pure extraction solvent is measured (I_0). Afterwards the extract of the oil-in-water sample is measured (I). From both measurements the absorption (A) can be calculated according to Beer's law. The absorption is directly proportional to the analyte concentration (c) multiplied by a wavelength dependent constant (α) and the path length of the sample cuvette (l):

$$A(\lambda) = -\log\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \alpha(\lambda) \times c \times l$$

α defines how intense light is absorbed by a sample molecule at different wavelengths. Hence, it defines the shape of the absorption spectrum seen in figure 1. However, α is usually unknown and therefore a calibration curve is used to establish the relation between the measured absorption and the sample concentration at a fixed path length of the measurement cell.

The transmission characteristic of the optical filter needs to be adapted to the spectral features of the analyte so that no interferences with the sample solvent occur. Figure 2 shows the spectrum of four different crude oil samples in the CH$_3$ deformation vibration region, measured with an FTIR spectrometer. A non-dispersive instrument, however, cannot read the exact absorption spectrum as plotted in figure 2. It only measures an average absorption reading depending on the transmission characteristic of the optical filter (black curve in figure 2). It is obvious from figure 2 that the central wavelength and the width of the optical filter need to be adjusted to the sample itself. For this application only the light in the CH$_3$ absorption region should pass through the sample and onto the detector. Signals from the extraction solvent on the other hand have to be completely blocked.

Because the filter-based instrument only reads an average value the choice of calibration substance is important too. The absorption signal of the calibration substance should resemble the sample as good as possible. In many measurement scenarios of oil-in-water concentrations the exact composition of the actual contaminant is unknown. Therefore it is not possible to calibrate the instrument to this exact analyte. The way forward is to choose a substance or a mixture of substances that resembles the absorption characteristic of suspected analytes best. From figure 2 it can be seen that typical crude oils have their absorption maximum around 1378 wavenumbers (reciprocal wavelength) and a shoulder around 1365 cm^{-1}. This shoulder is caused by branched CH$_3$ groups in sample molecules. This needs to be taken into account when choosing the calibration mixture used to calibrate the analytical method. Our examinations showed that a mixture of octane (straight molecule with two CH$_3$ groups) and iso-octane (5 branched CH$_3$ groups) suits crudes from low to high densities best and also works well for refined products. Figure 3 shows the response of the analyzer to aqueous samples that were spiked with 100 mg of different crude oils. Every sample was extracted with cyclohexane and then measured. In the ideal case the response of the analyzer would be exactly 100 mg for every sample. However, due to differences between the complex crude oil mixtures and the calibration mixture an expected deviation is observed for every sample. These deviations are small which verifies the applicability of this calibration mixture for oil-in-water measurements.

Single Lab Study

A new measurement technique always has to prove itself against established methods. As already discussed in the introduction the absolute concentrations measured will always vary from one method to the other. However, it is possible to correlate them to each other for a defined sample set. In a single lab study a precision statement has to be developed which gives indications on how well a chosen method can repeat measurement results over a certain concentration range and for different sorts of samples. The second relevant parameter of such a study is the method detection limit (MDL) – the lowest concentration that can be measured with the method.

To obtain the precision data 8 unique aqueous samples spiked with different crude oils at a total of six different concentration levels have been extracted. Afterwards the extracts were measured directly to get TOG values. Afterwards a second portion of every extract was measured after filtration over Florisil to obtain a TPH reading as well. The results are summarized in tables 1 and 2. Please note that for the TPH results at high concentrations Oil3 was replaced with Oil2 as its grease content exceeded the retention capacity of the used Florisil cartridges.

Pooling the data obtain for TOG and TPH measurements of extracted aqueous samples the below relative standard deviations can be given for each concentration level:

C (mg/l)	σ_{rel} (%) – TOG	σ_{rel} (%) – TPH
5	3.6	5.8
10	2.6	5.1
50	1.9	3.1
200	1.1	1.9
500	1.8	2.5

The method detection limit (MDL) was calculated according to 40 CFR Pt. 136, Appendix 2 from the measurement of 8 samples of ocean substitute water spiked with nominal concentrations of 1.7 mg/l of Oil3. The resulting MDLs for TOG and TPH are summarized below:

	TOG	TPH
MDL (mg/l)	0.48	0.34

Another important aspect that was evaluated during our single lab study was extraction time. Usually the aqueous sample is mixed with the extraction solvent and then shaken for a defined period of time. The longer this extraction time is the more tedious the analysis method is in total. We therefore evaluated the recovery rates of spiked oil samples from its aqueous sample matrices using cyclohexane as extraction solvent. A very heavy and a very light crude oil were used to cover a wide range of real world samples. Measured data is summarized in table 3. An extraction time of 30 seconds was not enough to complete extraction. Extending it to 90 seconds gave sufficiently enough recovery rates. What can be seen from the data too is that the recovery rate for light samples is lower than for the heavy sample. One possible explanation therefore is that the lightest components are lost during the extraction as they move to the gaseous phase. This loss, however, affects every extraction-based method the same way.

Summary

The measurement data shown above document that the newly developed oil-in-water measurement technique outperforms all currently used measurement techniques. Recently, a draft outlining the described above was submitted to ASTM to obtain a measurement standard. The use of a readily available solvent, which is environmentally safe too, in combination with a cost-effective measurement technique will help to bring the ease of use and analysis speed of IR spectroscopy back to labs around the world. With an extraction time below 2 minutes and the possibility to automate the extraction step through Florisil the total analysis time of oil-in-water samples is less than 10 minutes using eralytics' newly developed analyzer ERACHECK ECO.

[1] DOI:10.1016/S1001-0742(09)60276-X

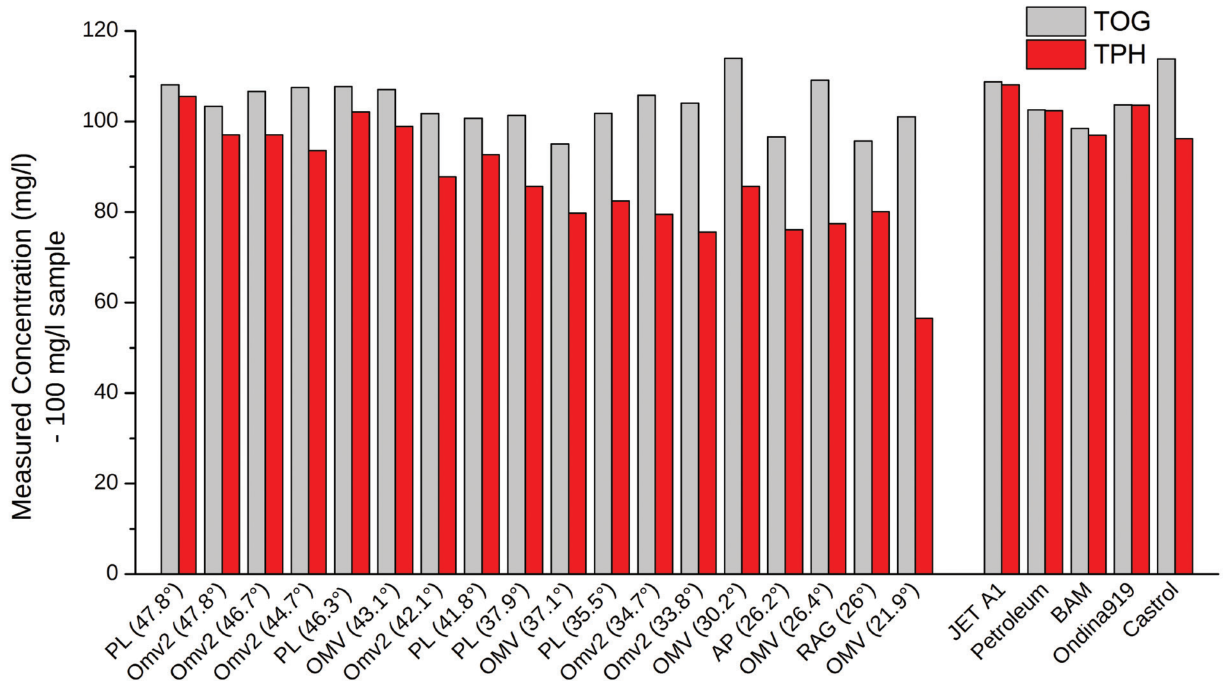

Figure 3: Measurement results for crude oils ranging from light to heavy crudes. The difference between the TOG and the TPH value results from the filtration loss over Florisil absorbing polar substances. On the right side of the graph some refined products are plotted as well. They typically show little to no loss during filtration.

Table 1: Total Oil and Grease (TOG) results. Every mean value consists of 8 independently extracted aqueous samples spiked with crude oil at the denoted concentration.

TOG	C mg/L	Mean	σ	Recovery (%)
blank	0	0.07	0.19	-
Oil 1	5	4.6	0.17	91
Oil 3	5	5.0	0.17	100
Oil 1	10	10.2	0.29	102
Oil 3	10	10.2	0.22	102
Oil 1	50	49.4	1.04	99
Oil 3	50	52.1	0.91	104
Oil 1	200	202.1	2.6	101
Oil 2	200	189.3	1.8	95
Oil 1	500	493.7	10.4	99
Oil 2	500	487.0	6.8	97

Table 2: Total Petroleum Hydrocarbon (TPH) results. Every mean value consists of 8 independently extracted aqueous samples spiked with crude oil at the denoted concentration and filtrated over Florisil. The "TPH/TOG (%)" values show the percentage of sample that was measured after the filtration step. The difference to 100% is considered grease.

TPH	C mg/l	Mean	σ	TPH/TOG (%)
blank	0	-0.08	0.19	-
Oil 1	5	4.1	0.28	89
Oil 3	5	3.6	0.14	72
Oil 1	10	8.4	0.48	82
Oil 3	10	6.9	0.30	68
Oil 1	50	44.3	1.05	90
Oil 3	50	36.7	1.4	70
Oil 1	200	185.7	2.1	92
Oil 2	200	158.5	4.1	84
Oil 1	500	461.7	15.1	94
Oil 2	500	419.9	3.1	86

Table 3: Result of extraction experiments of two types of crude oil. The same sample was prepared 8 times as a spiked aqueous sample and then extracted with cyclohexane. The sample was shaken vigorously for 30 seconds or 3 times 30 seconds without opening the extraction flask.

Heavy crude – API 26.4°		Light crude – API 43.1°	
1x30 sec	3x30 sec	1x30 sec	3x30 sec
94.28 %	98.21 %	95.55 %	96.91 %
96.20 %	98.95 %	94.25 %	97.35 %
94.47 %	98.49 %	96.60 %	95.58 %
93.05 %	97.82 %	94.38 %	96.12 %
97.07 %	98.70 %	95.51 %	93.78 %
95.66 %	Outlier	93.39 %	93.73 %
98.22 %	101.59 %	90.97 %	94.64 %
96.35 %	99.36 %	91.47 %	95.95 %
Avg: 95.66 %	Avg: 99.02 %	Avg: 94.02 %	Avg: 95.51 %

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