Environmentally Friendly FTIR Spectroscopy for Analysis of Oil in Water

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Crude oil consists of a mixture of hydrocarbons (HCs) with different chemical compositions, but most exists as long chain HCs (e.g., mineral oil, naphthalenic and paraffinic), aromatics, and lighter short chain HCs. The aromatics and short chain HCs are commonly referred to as 'lights' and are more miscible in water than long chain HCs. Long chain HCs are particularly harmful to the environment due to their persistence in water and their tendency to form layers on top of water.

A wide variety of methods are available for the measurement of oil in water. Gas chromatography with flame ionisation detection (GC-FID) is considered to be the most accurate method for oil in water. It is highly accurate and sensitive for volatile, low-molecular-weight compounds, but it can be less effective than Fourier transform infrared (FTIR) measurement for high-molecular-weight compounds such as paraffins and heavy napthalenes.

FTIR based liquid-liquid extraction methods measure both the lights and heavier long chain HCs. In addition, today's FTIR spectrometers are both sensitive and portable, allowing onsite analysis of oil in water in any location – including offshore rigs.

Here we present an environmentally friendly method for analysis of oil in water by FTIR spectroscopy, based on the American Society for Testing and Materials (ASTM) D7678-11.[1] Cyclohexane is used as the solvent, replacing the halogenated solvents that feature in ASTM D3921 and ASTM D7766-04 (freon and fluorinated trimer [S-316]). Many halogenated solvents typically used in FTIR methods are expensive (plus have disposal costs) or require a special permit to use. Freon has been banned by the Montreal protocol due to its ozone depleting activity.

This FTIR version of the ASTM D7678 features a limit of detection (LOD) of 0.25mg/L (0.25ppm) and a limit of quantification (LOQ) of 0.75mg/L (0.75ppm) oil in water with an upper limit at 1000mg/L (1000ppm).

The method measures the methyl group absorbance at 1370–1380 cm^{-1} (7.25–7.30 microns) present in both the HCs and the lighter aromatics in crude oil (such as toluene, xylenes, and ethylbenzene). Generally any hydrocarbon containing a methyl group will absorb in this region. Cyclohexane has no methyl groups and thus makes it a suitable solvent for this analysis. The results is that, as the IR spectrum of cyclohexane has no absorbance at 1378 cm^{-1}, any oils collected in the cyclohexane during extraction will add to the absorbance at 1378 cm^{-1}. This absorbance increase is proportional to the concentration of oil and can be precisely calibrated (as shown later).

A filtration step with silica gel or Florisil is required to remove any grease. The HC value achieved before clean-up with Florisil is referred to as total oil and grease (TOG) and the HC value after the extract is filtered with Florisil is the total petroleum hydrocarbon (TPH).

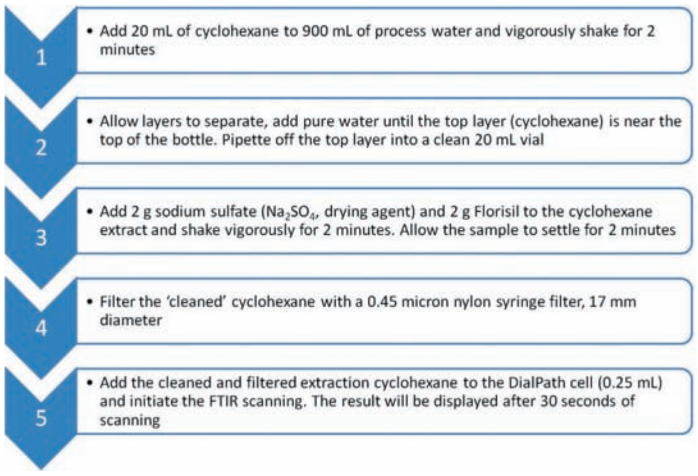
The ASTM D7678 based oil in water FTIR calibration and results described here will correlate to ASTM D3921, D7066, ISO 9377-2, EPA 413.2, and EPA 418.1 methods. Note that, since there are differences in the calibration mixtures of this method relative to others, appropriate correction factors may be necessary to relate the results to the ASTM 7678-11 calibration as detailed in Note 2 of ASTM 7678-11.[1] These correction factors can be applied in the Agilent MicroLab software.

Method and Materials

An acidified or non-acidified 900mL sample of water or wastewater was extracted with 20mL of cyclohexane. The non-polar material extracted into the cyclohexane (TPH) was measured by mid-infrared spectroscopy (1000µm pathlength) which was achieved using the DialPath accessory on an Agilent Cary 630 FTIR spectrometer. All glassware that will contact the sample should be thoroughly cleaned, rinsed with distilled water and dried at 130°C. Prior to starting this procedure, the glassware should be rinsed with clean (pure) cyclohexane solvent and dried. This method recommends a wide mouth 1 L sample bottle with a fluoropolymer liner or a wide-necked glass flask with a ground neck with either a glass or fluoropolymer stopper. The process water sample should be collected directly, per ASTM Practice D3370, with the 1 L sample bottle and the extraction with the 20mL of cyclohexane should be performed in this same sample bottle.

Acidification with hydrochloric acid should, according to ASTM D7678, be performed to preserve the sample. However, validation samples using this method without acidification have been found to have excellent results if the extraction is performed quickly enough. Any grab sample not acidified and run with this method should be extracted within 1–2 days for best results.

The simple and speedy process optimisation procedure, requiring minimal preparation to achieve accurate results, is described in *Figure 1*.



1 • Add 20 mL of cyclohexane to 900 mL of process water and vigorously shake for 2 minutes

2 • Allow layers to separate, add pure water until the top layer (cyclohexane) is near the top of the bottle. Pipette off the top layer into a clean 20 mL vial

3 • Add 2 g sodium sulfate (Na_2SO_4, drying agent) and 2 g Florisil to the cyclohexane extract and shake vigorously for 2 minutes. Allow the sample to settle for 2 minutes

4 • Filter the 'cleaned' cyclohexane with a 0.45 micron nylon syringe filter, 17 mm diameter

5 • Add the cleaned and filtered extraction cyclohexane to the DialPath cell (0.25 mL) and initiate the FTIR scanning. The result will be displayed after 30 seconds of scanning

Figure 1. The process optimisation procedure.

Calibration and Validation

Calibration standards were prepared by weight with a Base 20 light mineral oil from Spex Certiprep, with concentrations from 0 to 1465mg/L in cyclohexane. These standards translate to the 0–32.55mg/L oil in water concentration range *(Table 1)*. Each calibration standard was measured twice on the Cary 630 FTIR.

The enrichment factor of 45 is used to calculate the calibration concentrations, as described in ASTM D7678,[1] for a 20 L cyclohexane extraction from 900mL of process water. The spectra of the calibration standards were correlated using a partial least squares (PLS) algorithm from 1370–1380cm^{-1}; automated data analysis with multivariate algorithms is acceptable as per note 5 of ASTM D7678.[1] Results from this calibration are shown in *Figure 2*, showing the final oil in water values. The correlation of the actual versus predicted curve for the calibration has an excellent correlation of $R^2 = 0.99929$.

Table 1. The calibration set prepared and analysed for oil in cyclohexane.

Oil calibration set	
Standard name	**Oil (mg/L)**
OIW Soln A	0.00
OIW Soln B	0.05
OIW Soln C	0.15
OIW Soln D	0.26
OIW Soln E	0.84
OIW Soln F	1.70
OIW Soln G	2.54
OIW Soln H	4.20
OIW Soln I	8.30
OIW Soln J	16.54
OIW Soln K	24.90
OIW Soln L	32.55

The Oil in Water Method Validation

Two validation standards – a high and a low standard - were prepared to test the precision, accuracy and percent recovery of this method. Solution A was a high standard at 9.3mg/L mineral oil and 5mg/L grease in water and Solution B was a low standard at 1.4mg/L mineral oil and 0.7mg/L grease in water. The standards were extracted and prepared with the extraction

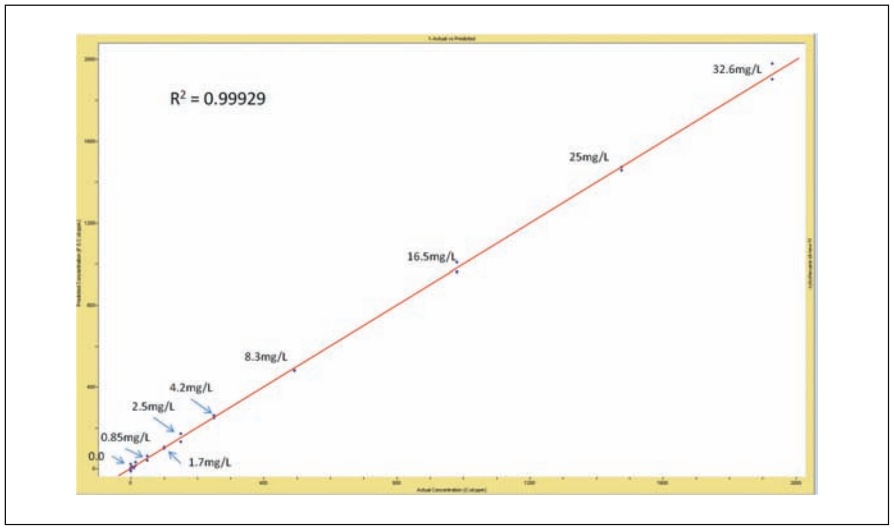


Figure 2. The mineral oil in cyclohexane calibration plot of actual (X-axis) versus predicted (Y-axis) values. The values displayed are the final concentrations of oil in water based on the ASTM D7678 parameters (900mL water, 20mL

and filtration procedures, as described above. Each solution was measured four times. The results *(Table 2)* indicate excellent precision based on the low relative standard deviations. The relative standard deviation was just 2.69% for the high standard, and still very good - 5.69% - for the low standard. The analogous validation standard published in the ASTM D7678 was 2.41% relative standard deviation (RSD) with a 10mg/L standard; lower levels in fresh water extractions were not shown. The ASTM oil in water precision for a 10mg/L sample, extraction from ocean substitute water, has a 3.59% RSD and a 5mg/L oil standard with a 9.47% RSD. This FTIR method offers similar precision at the 10mg/L level, and observed better precision at the 5mg/L level based on this methods equal performance (data shown in *Table 2*, 5.69% RSD) at one fifth the concentration.

Recoveries were calculated at 101% for the high standard and 103% for the low standard. ASTM D7678 reported recoveries of 132% and 144% for the 10mg/L and 5mg/L samples respectively. The difference in the recoveries likely lies in the fact that the results presented in the ASTM method used tetradecane, causing a high prediction compared to the mixed mineral oils used in the validation. Regardless, recoveries found in this test showed that both the extraction and calibration procedure were accurate.

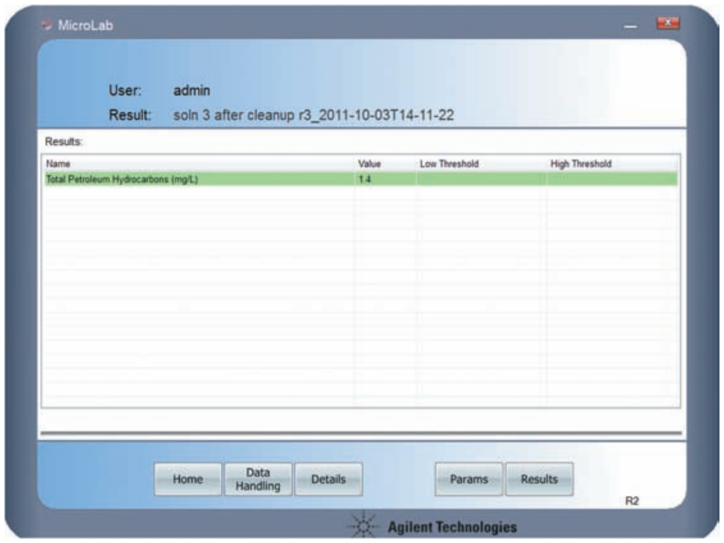
Table 2. The oil in water results for high and low validation standards in non-acidified water created with 9.3mg/L (Solution A) and 1.4mg/L (Solution B) mineral oil respectively, followed by the extraction with cyclohexane. The samples are measured in quadruplicate.

	TPH	
	Solution A	**Solution B**
Run 1	9.70	1.34
Run 2	9.43	1.54
Run 3	9.12	1.44
Run 4	9.60	1.46
Mean value	9.46	1.45
Standard deviation	0.24	0.08
Relative standard deviation	2.69	5.69
% recovery	101.7	103.2

FTIR Software for Ease of Use

Agilent Technologies MicroLab FTIR software offers a method with the necessary calibration files pre-installed for use with the FTIR spectrometer used in this application. The method is designed to walk the user through the complete measurement, presenting the quantitative result at the end. This makes the entire system easy to use for almost any skill level user.

After following the sample preparation steps in ASTM D7678, the cyclohexane top layer is removed and analysed on the unique DialPath liquid cell. This produces the accuracy of sealed cells in an easy-to-use and easy-to-clean design. An example of the results screen from the software for the low validation standard is shown in *Figure 3*.



User: admin
Result: soln 3 after cleanup r3_2011-10-03T14-11-22

Results:

Name	Value	Low Threshold	High Threshold
Total Petroleum Hydrocarbons (mg/L)	1.4		

Figure 3. The automatically generated data results from the MicroLab software for FTIR spectrometers. The TPH value is obtained after a clean-up filtration to remove grease. This result is from a validation standard of 1.4mg/L mineral oil and 0.7mg/L vegetable oil in fresh water, which was extracted with 20mL cyclohexane and filtered.

Conclusions

Here we demonstrate the applicability of the recently released ASTM D7678 oil in water method using a portable mid-infrared FTIR spectrometer, resulting in equivalent performance but with the added practically of a portable system. By selecting a non-halogenated solvent to extract and measure the oil in water in the 0.85–1000mg/L range, this method is environmentally friendly and offers cost savings against other FTIR ASTM oil in water methods.

The calibration used in this method indicates excellent correlation to mineral oil concentrations. Results from validation standards indicate as good or better performance than the published ASTM D7678 validation results. The sample preparation procedures are simplified to five practical steps that can be performed out of the lab. By selecting a new-generation, reliable and field-proven portable FTIR spectrometer, excellent performance and reproducibility can be achieved on or offsite.

Reference

1. ASTM D7678 - 11 Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy. Available via: http://www.astm.org/Standards/D7678.htm

Frank Higgins received his Bachelor of Science degree in biology, chemistry conc., from Florida Southern College (FSC) in 1998. After college Frank gained experience and expertise in the focused area of vibrational spectroscopy and interpretation of mid-infrared and Raman spectra at Cytec Industries as a Research Chemist. Eight years later Frank moved into the portable and handheld FTIR instrument industry through employment with A2 Technologies (now Agilent Technologies) as an Applications Development Scientist. Currently, thermal damage of composites, polymer analysis, and oil in water analysis are priority areas being studied and developed for mobile FTIR at the now Agilent Technologies Danbury Connecticut location for Mobile Spectroscopy products.