



Environmentally friendly oil in water analysis by FTIR spectroscopy, based on ASTM D7678-11

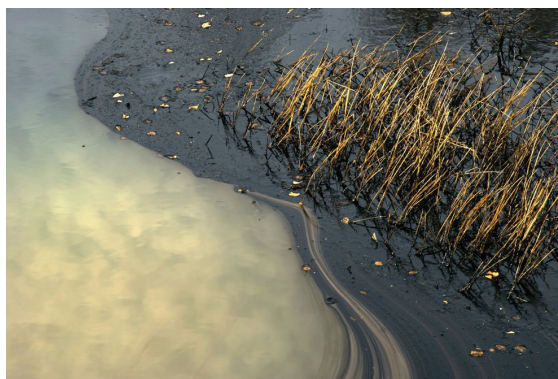
Application note

Environmental; Energy and fuels

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Introduction

Infrared (IR) spectroscopy has been used for measuring the amount of oil in water for many years. Recent advances in Fourier transform infrared (FTIR) spectrometers allow them to be both sensitive and portable, making onsite analysis of oil in water possible. These new capabilities are ideal for use at oil depots, refineries, offshore rigs, and environmental remediation sites. The method detailed in this application note is based on the ASTM D7678-11. This method uses cyclohexane as the solvent, replacing halogenated solvents such as Freon and fluorinated trimer (S-316), which are used in ASTM D3921 and ASTM D7066-04 respectively. 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 0.25 mg/L (0.25 ppm) and a limit of quantification (LOQ) of 0.75 mg/L (0.75 ppm) oil in water with an upper limit at 1000 mg/L (1000 ppm). The standard procedures for liquid-liquid solvent extraction of hydrocarbons from water remain unchanged from previous ASTM methods. 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.



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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 D7678-11 calibration as detailed in Note 2 of ASTM D7678-11. These correction factors can be applied in the Agilent MicroLab software.

Composition and measurement of oil (TPH) and total oil and grease (TOG) in cyclohexane

Crude oil is a mixture of hydrocarbons (HCs) with different chemical compositions, but most of crude oil exists as long chain HCs (mineral oil, naphthalenic and paraffinic), aromatics, and lighter short chain HCs. The FTIR spectra of a common mineral oil and crude oil are shown in Figure 1. The aromatics and short chain HCs are commonly referred to as 'lights' and are more miscible in water than long chain HCs. FTIR based liquid-liquid extraction methods, such as this one, measure both the lights and heavier 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. This FTIR 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). The localized baseline used to measure the 1378 cm^{-1} peak in this method is shown in the mineral oil spectrum (Figure 1). Generally any hydrocarbon containing a methyl group will absorb in this region. Cyclohexane has no methyl groups and thus makes a suitable solvent for this analysis. The IR spectrum of cyclohexane, shown in Figure 2, has no absorbance at 1378 cm^{-1} . Any oils collected in the cyclohexane during extraction will add to the absorbance at 1378 cm^{-1} , as shown in the expanded region of Figure 2. This absorbance increase is proportional to the concentration of oil and can be precisely calibrated (as shown later). EPA 1664 and other previous EPA, ASTM, and ISO FTIR methods for oil in water require a filtration step with silica gel or Florisil to remove any grease. In this method, the nominal total oil and grease (TOG) is the HC value before clean-up with Florisil. The total petroleum hydrocarbon (TPH) is the value measured after the extract is filtered with Florisil.

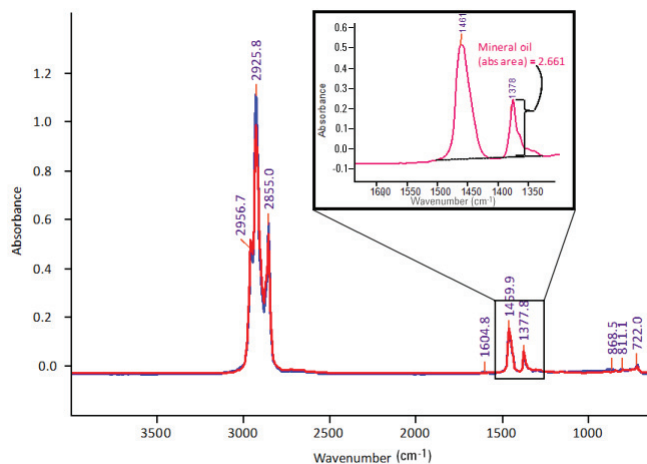


Figure 1. The overlaid FTIR spectra of crude oil (blue) and mineral oil (red). The zoomed region indicates the local baseline (dashed line) used for the 1378 cm^{-1} peak area measurement by FTIR.

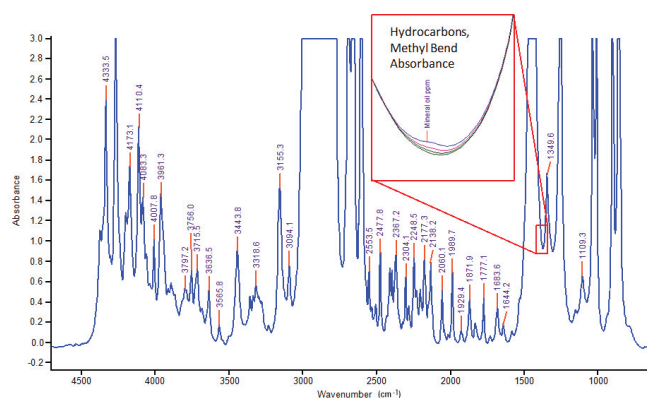


Figure 2. The FTIR spectrum of cyclohexane measured on the Agilent 4500 FTIR spectrometer with a DialPath accessory. The inset zoom box illustrates the overlaid spectral region of measurement of the hydrocarbons (showing calibration standards 0–33 mg/L) using the methyl absorbance at 1378 cm^{-1} .

Cyclohexane extraction: oil FTIR calibration

Test method, apparatus, and materials

An acidified or non-acidified 900 mL sample of water or wastewater was extracted with 20 mL of cyclohexane. The non-polar material extracted into the cyclohexane is referred to as total petroleum hydrocarbons (TPH) and was measured by mid-infrared spectroscopy using the DialPath or TumbIIR accessory (1000 μm pathlength) on an Agilent 4500 or 5500 series FTIR spectrometer. All glassware that will contact the sample should be thoroughly cleaned, rinsed with distilled water and dried at 130 $^{\circ}\text{C}$. 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 20 mL of cyclohexane should be performed in this same sample bottle. Following ASTM D7678, acidification with hydrochloric acid should be performed to preserve the sample; however, it is optimal for this method to extract the sample soon after collection. 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 onsite or routine process optimization oil in water procedure described here is fast, simple, and requires the minimal sample preparation necessary to achieve accurate oil in water results. The simple five step process summary is:

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 or TumbIIR cell (0.25 mL) and initiate the FTIR scanning. The result will be displayed after 30 seconds of scanning.

Calibration and validation

A calibration of mineral oil in cyclohexane was created using 11 non-zero points (Table 1). Each calibration standard was measured twice. The calibration standards were prepared by weight with a Base 20 light mineral oil from SPEX Certiprep, with concentrations from 0 to 1465 mg/L in cyclohexane. These standards translate to the 0–32.55 mg/L oil in water concentration range (Table 1). The enrichment factor of 45 is used to calculate the calibration concentrations, as described in ASTM D7678, for a 20 L cyclohexane extraction from 900 mL of process water. The spectra of the calibration standards were correlated using a partial least squares (PLS) algorithm from 1370–1380 cm^{-1} ; automated data analysis with multivariate algorithms is acceptable as per note 5 of ASTM D7678. Results from this calibration are shown in Figure 3, 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 analyzed for oil in cyclohexane. The values shown are the final concentrations based on 900 mL of process water extracted with 20 mL of cyclohexane. The enrichment factor of 45 is used in the calculation, as defined in the ASTM D7678 method.

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

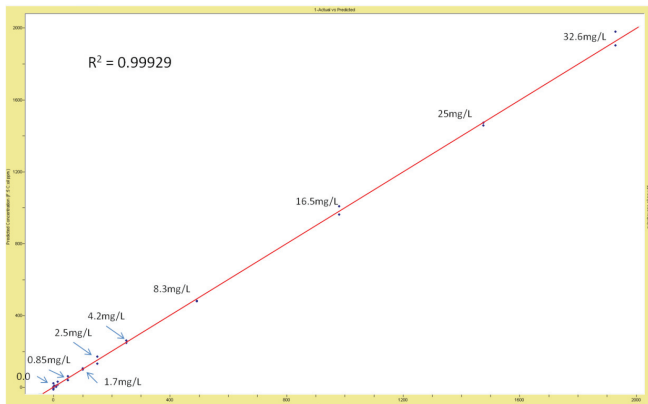


Figure 3. The mineral oil in cyclohexane calibration plot of actual (X-axis) versus predicted (Y-axis) values. The values displayed are the final concentrations of oil in water based on the ASTM D7678 parameters (900 mL water, 20 mL cyclohexane).

The oil in water method validation

Two validation standards were prepared to test the precision, accuracy and percent recovery of this ASTM D7678 based method on the Agilent 4500 or 5500 FTIR. The first validation standard (Solution A) was a high standard at 9.3 mg/L mineral oil and 5 mg/L grease in water. The second validation standard (Solution B) was a low standard at 1.4 mg/L mineral oil and 0.7 mg/L grease in water. The standards were extracted and prepared with the above extraction and filtration procedures. The solutions were measured four times each and the TPH results are shown in Table 2. The results indicate excellent precision based on the low relative standard deviations. As expected the relative standard deviation is lowest in the high standard 2.69%, but still very good for the low standard at 5.69%. The analogous validation standard published in ASTM D7678 (Table 3) indicates a 2.41% relative standard deviation with a 10 mg/L standard; lower levels in fresh water extractions were not shown in the ASTM method. The ASTM oil in water precision for a 10 mg/L sample, extraction from ocean substitute water, has a 3.59% relative standard deviation and a 5 mg/L oil standard with a 9.47% relative standard deviation. This Agilent FTIR method indicates similar precision at the 10 mg/L level, and observed better precision at the 5 mg/L level based on this methods equal performance (data shown in Table 2, 5.69% relative standard deviation) 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 10 mg/L and 5 mg/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 9.3 mg/L (Solution A) and 1.4 mg/L (Solution B) mineral oil respectively, followed by the extraction with cyclohexane. The samples are measured in quadruplicate with the Agilent DialPath accessory.

	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

Measurement with Agilent MicroLab FTIR software

A method is available for the Agilent MicroLab FTIR software, which has the calibration files pre-installed. This is suitable for use with the Agilent 4500 and 5500 FTIR, each using the DialPath or TumbIIR sampling interface with a pathlength of 1000 microns. Like all component methods in the MicroLab FTIR software, this 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 analyzed on the unique DialPath or TumbIIR liquid cell. The DialPath and TumbIIR produce the accuracy of sealed cells in an easy-to-use and easy-to-clean design. Examples of the results screens from the MicroLab software for the high and low validation standards are shown in Figures 4 and 5.

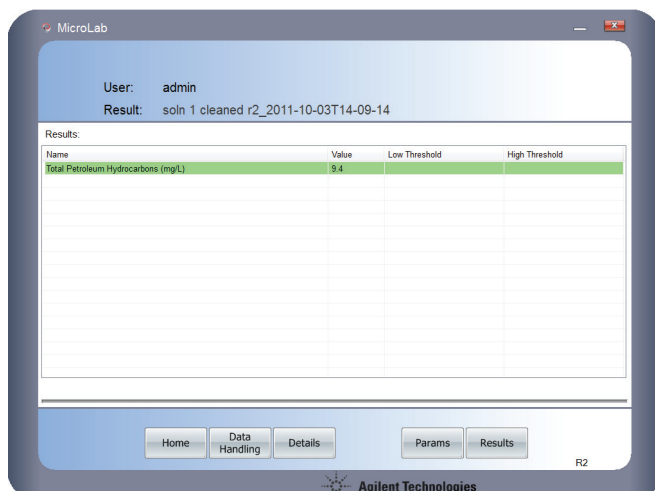


Figure 4. The automatically generated data results from the MicroLab software for the Agilent 4500 series, and 5500 series FTIR spectrometers. The total petroleum hydrocarbon (TPH) value is obtained after a clean-up filtration to remove grease. This result is from a validation standard of 9.3 mg/L mineral oil and 5 mg/L vegetable oil in fresh water (Table 2), which was extracted with 20 mL cyclohexane and filtered.

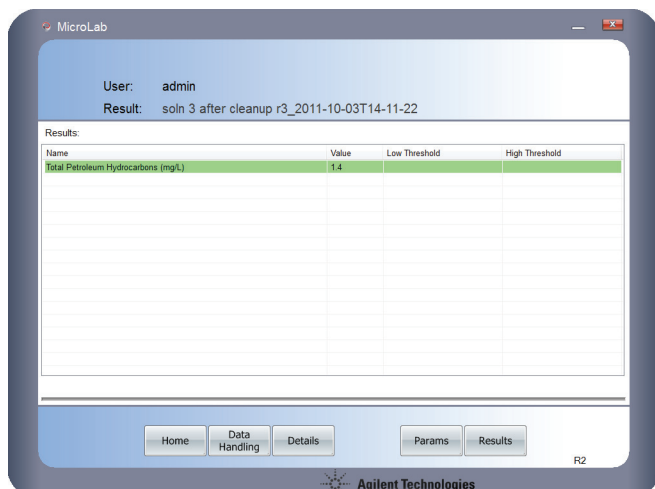


Figure 5. The automatically generated data results from the MicroLab software for the Agilent 4500 series, and 5500 series FTIR spectrometers. The total petroleum hydrocarbon (TPH) value is obtained after a clean-up filtration to remove grease. This result is from a validation standard of 1.4 mg/L mineral oil and 0.7 mg/L vegetable oil in fresh water (Table 2), which was extracted with 20 mL cyclohexane and filtered.

Cyclohexane extraction compared to other oil in water measurement methods

Many methods exist for measurement of oil in water using both infrared spectroscopy and other techniques. The method presented here compares favorably to these other methods for a variety of different reasons. Gas chromatography with flame ionization detection (GC-FID) is generally considered the most accurate method for oil in water. It is specified in ISO 9377-2. It is highly accurate and sensitive for volatile, low molecular weight compounds, but it can be less effective than FTIR measurement for high molecular weight compounds such as paraffins and heavy naphthalenes.

A wide variety of FTIR methods have previously been published, many of which used Freon or other halogenated solvents. Methods still exist that use Freon 113 (1,1,2-Trichlorotrifluoroethane, TTE), tetrachloroethylene (perchloroethylene, PCE, TTCE), trichloroethylene (TCE, PERC), dimer/trimer of chlorotrifluoroethylene (S-316), and carbon tetrachloride (CCl_4). These solvents are used because they have no infrared absorbance near the hydrocarbon bands. Unfortunately, though most of these solvents either require a special permit, or are expensive to buy. Cyclohexane doesn't have as clean of a spectrum near the hydrocarbon bands, but there is a sufficient region in which to measure the hydrocarbon bending mode. Cyclohexane is also comparatively low cost; in the U.S. at the time of publishing, one liter of cyclohexane costs \$70. Comparatively, one liter of S-316 cost \$440, one liter of CCl_4 cost \$300, and one liter of TCE cost \$94. The cost per sample (solvent only) using this Agilent ASTM D7678 method is \$1.40/sample, compared to \$30/sample using the S-316 solvent for ASTM D7066-04. This assumes that the S-316 solvent is reused three times and 2 samples per day, which would reach \$20,000/year for the ASTM D7066-04 method. The above costs don't factor in the disposal costs for these halogenated solvents. FTIR methods using these restricted solvents are mostly considered "lab only", similar to the more complex gas chromatography method (ISO 9377-2).

Conclusions

Equivalency in performance and applicability to the recently released ASTM D7678 oil in water method has been demonstrated using Agilent's line of portable mid-infrared FTIR spectrometers, the 4500, and 5500 Series FTIR. This new ASTM method uses a more environmentally friendly non-halogenated solvent to extract and measure the oil in water in the 0.85–1000 mg/L range. The method provides the 'total petroleum hydrocarbons' and 'total oil and grease' values, with 21 times less cost per sample compared to 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.

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