APPLICATION NOTE

FT-IR Spectroscopy

Authors:

Kathryn Lawson-Wood

Ian Robertson

PerkinElmer, Inc.
Seer Green, England

FT-IR Quantification of Hydrocarbons in Environmental Water Samples Based on ASTM D7678

Introduction

Hydrocarbon sources in water are typically a result of human activity and measurement of their concentration in water supplies is important to maintaining human and environmental health. Hydrocarbons are a common and natural occurrence in water systems and ordinarily microbial decomposition of these compounds occurs naturally over time. However, increased concentrations resulting from industrial activities restrict this process. The resulting effects on the environment, which include formation of surface films and interference with aerobic and anaerobic biological processes.[1]

Mid-IR spectroscopy is an established technique for rapid hydrocarbon analysis in offshore oil operations and has recently experienced renewed interest for a variety of applications. There is increasing environmental concern over the use of halogenated solvent extraction techniques since they are harmful to the environment.

PerkinElmer®
For the Better

This application note illustrates the use of cyclohexane extraction of hydrocarbons coupled with Infrared (IR) transmission measurement to provide rapid and precise results with useful detection limits (sub-ppm) and a non-halogenated solvent.

Transmission Measurement with Cyclohexane Extraction

A liquid-liquid extraction (LLE) using a halogenated solvent is commonly used in IR spectroscopy for the quantification of hydrocarbons and relies on strong C-H stretch bands resulting in a low detection limit and high sensitivity. Hexane extraction with Attenuated Total Reflectance (ATR) measurement is another method that uses a non-halogenated solvent, but it cannot be used to detect volatile contaminants.

Cyclohexane extraction of hydrocarbons combined with transmission measurement is a less harmful alternative to halogenated solvent methods. Liquid cells with CaF_2 windows (Figure 1) are commonly used in transmission mode due to their low absorption coefficient and high damage threshold. The method shown in this application is based on ASTM D7678[2], which uses a cyclic aliphatic hydrocarbon to extract hydrocarbons in water samples and IR absorption measurement between 1370-1380 cm^{-1}.

Determination of the amount of hydrocarbons in water requires a concentration factor to be taken into account based on the volumes of solvent and sample used in the extraction process.In previous application notes, a concentration factor of 5 and a pathlength of 0.5 mm were used. In this application note, the concentration factor and pathlength were increased to 45 and 1.0 mm, respectively, resulting in a much improved detection limit.

The fundamental principle of this method takes advantage of the methyl deformation mode of hydrocarbons at 1377 cm^{-1} which, although weakly absorbing, is not present in the spectrum of cyclohexane making it a suitable solvent for this analysis. Using a fixed pathlength, the height of the absorption peak at 1377 cm^{-1} can be directly correlated to hydrocarbon concentration. Sensitivity is usually poorer in comparison with halogenated solvent methods due to the limited useable pathlength and weaker bands, but a useful detection limit sub-ppm is achievable.

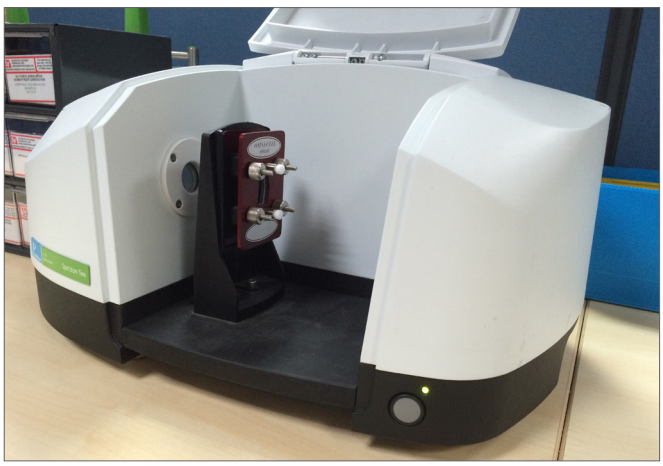

Figure 1. Transmission measurement on Spectrum Two™ with Specac Omni-Cell™.

Calibration Process

A stock solution of paraffin oil (2050 mg/L) was prepared in a 1L-volumetric flask by diluting a weighed amount of paraffin oil with cyclohexane. From this stock solution, a series of calibration standards within the concentration range 0 - 1350 mg/L paraffin oil were prepared in 50 mL volumetric flasks by dilution with cyclohexane. These standards were equivalent to the concentration range of 0 – 30 mg/L oil in water using the concentration factor of 45 (Table 1), as described in ASTM D7678 below.

Table 1. Calibration standards. Equivalent hydrocarbon concentrations in water are based on 450 mL water extracted with 10 mL cyclohexane giving a concentration factor of 45.

Standard	Hydrocarbon Concentration in oil (mg/L)	Equivalent Hydrocarbon Concentration in water (mg/L)
1	0.00	0.00
2	22.50	0.50
3	50.00	1.11
4	100.00	2.22
5	225.00	5.00
6	675.00	15.00
7	1350.00	30.00

Using a Spectrum Two™ FT-IR spectrometer, the IR spectra of the calibration standards were collected in transmission at the analytical wavelength of 1377 cm^{-1} using cyclohexane as a blank. This was achieved using a Specac liquid Omni-Cell with CaF_2 windows and a 1.0 mm pathlength. A 2 minute scan accumulation time and a resolution of 8 cm^{-1} was employed on Spectrum® software. In between the sampling of each standard, the cell was cleaned by flushing with cyclohexane. A calibration graph was constructed by applying a Beer's Law algorithm in Spectrum Quant™ using the height of the absorption peak at 1377 cm^{-1} from the baseline at 1396 cm^{-1}.

Results

Spectra and calibration curve of the paraffin oil standards are shown in Figures 2 and 3, respectively. The linear regression coefficient (R^2) obtained from the calibration curve, displayed in Figure 3, is greater than 0.999 indicating a high level of data correlation. The standard error of prediction (SEP) is 0.16 and taking the limit of detection (LOD) as 5 x SEP, the LOD is around 0.8 mg/L. However, this takes into account standard-preparation errors and in practice a smaller LOD may be expected.

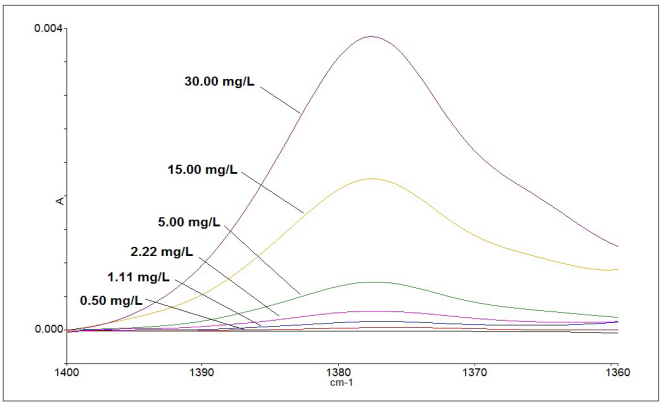

Figure 2. Spectra of paraffin oil calibration standards.

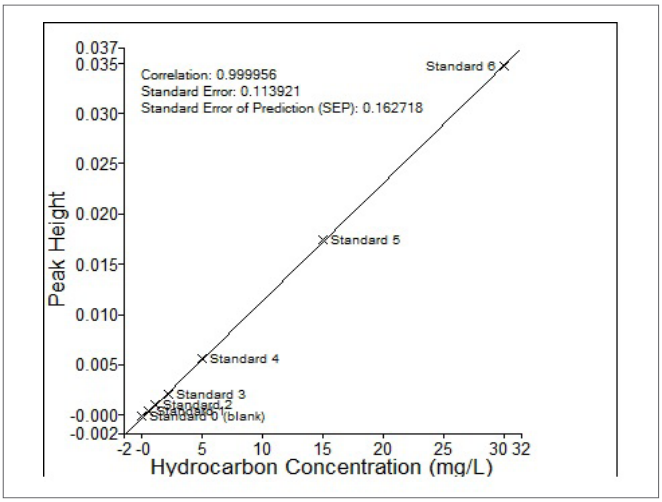

Figure 3. Calibration curve of paraffin oil standards in terms of concentration in water.

Method Validation

Spiked water samples (5.99 mg/L and 12.40 mg/L paraffin oil) were prepared as validation standards to test the accuracy and precision of this method. This was achieved by diluting known masses of paraffin oil with 450 mL deionised (DI) water in a 500 mL screw capped sample bottle and extracting with 10 mL cyclohexane by following the ASTM D7678 method.[2]

ASTM D7678 Method:

1. Add 10 mL cyclohexane to 450 mL of the spiked water sample in a screw-capped sample bottle.
2. Cap the bottle and shake vigorously for two minutes.
3. Allow the phases to separate and remove the majority of the top layer (cyclohexane) from the sample bottle.
4. Add approximately 1 g sodium sulphate (Na_2SO_4, drying agent) to remove any water
5. Calculate the concentration factor by dividing the original sample volume (450 mL) by the solvent volume (10 mL) as shown in Equation 1 below.

$$\text{Concentration Factor} = \frac{\text{Sample volume (450 mL)}}{\text{Solvent volume (10 mL)}} = 45$$

Equation 1. Concentration factor calculation.

Repeat measurements were performed on each extracted sample to determine the repeatability of the results. This was achieved by injecting the sample into the liquid cell and scanning it three times. The sample was then removed and the process repeated twice more, resulting in nine measurements as shown in Table 2. Mean calculated hydrocarbon content is reported in terms of hydrocarbon concentration in water. The overlaid spectra of the repeat measurements for the 5.99 mg/L and 12.40 mg/L spiked samples are shown in Figures 4 and 5, respectively.

Based on the relative standard deviations (RSD), the results suggest good levels of precision in comparison with the ASTM D7678 method. ASTM D7678 reports RSD values of 9.47% and 3.59% for 5.0 mg/L and 10.0 mg/L validation standards, respectively. As expected, the validation sample of highest concentration (spike 2) had the lowest RSD of 2.86% suggesting a good level of precision while the lowest concentration (spike 1) had the highest RSD of 6.30%, a reasonable level of precision.

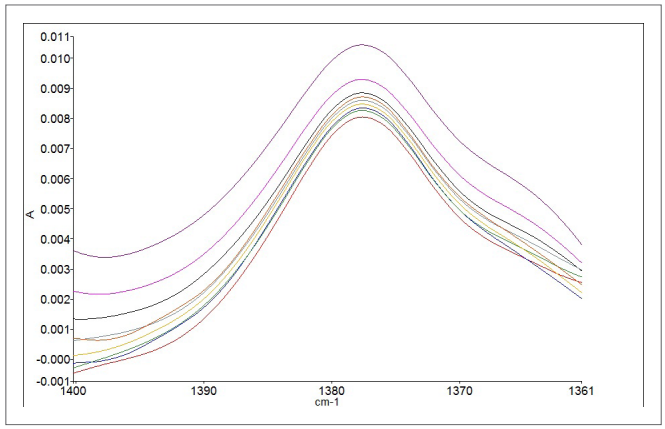

Figure 4. Overlaid 5.99 mg/L spike 1 sample spectra.

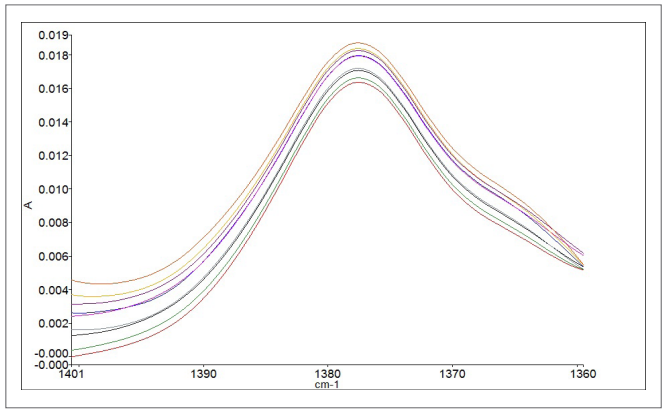

Figure 5. Overlaid 12.40 mg/L spike 2 sample spectra.

Table 2. Repeatability measurements for spike samples.

Sample	Actual Hydrocarbon Concentration in water (mg/L)	Number of Measurements	Mean Calculated Hydrocarbon Concentration in water (mg/L)	Standard Deviation (mg/L)
Spike 1	5.99	9	6.67	0.42
Spike 2	12.40	9	12.93	0.37

Measurement of Effluent Samples

A water sample collected from an industrial effluent stream was filtered and extracted using the same ASTM D7678 method. Repeat spectra of the sample were recorded using the same approach as the validation samples and the mean hydrocarbon content calculated. The overlaid spectra of the repeat measurements are shown in Figure 6 with the calculated hydrocarbon content shown in Table 3. The mean hydrocarbon concentration in water was determined to be 4.36 mg/L with a relative standard deviation of 1.85%, indicating a very good level of repeatability.

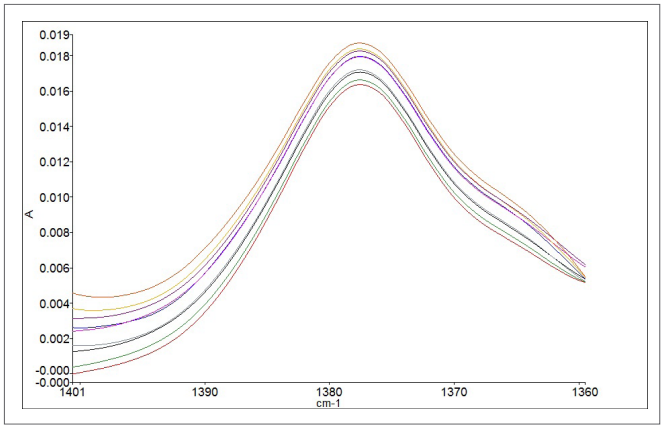

Figure 6. Overlaid effluent sample spectra.

Table 3. Results for effluent sample.

Sample	Number of Measurements	Mean Calculated Hydrocarbon Concentration in water (mg/L)	Standard Deviation (mg/L)
Effluent sample	9	4.36	0.08

Simplifying the Measurement Process Using PerkinElmer's Spectrum Touch™ Software

Quantitative results can be achieved using a Spectrum Touch method specifically designed to perform this hydrocarbon analysis. Spectrum Touch methods are aimed at routine operators to achieve rapid results and encompass a simple interface to walk the user through as shown in Figure 7. Starter calibration files are pre-installed into the method and the user simply follows the sample preparation steps in ASTM D7678 and the guided Spectrum Touch workflow.

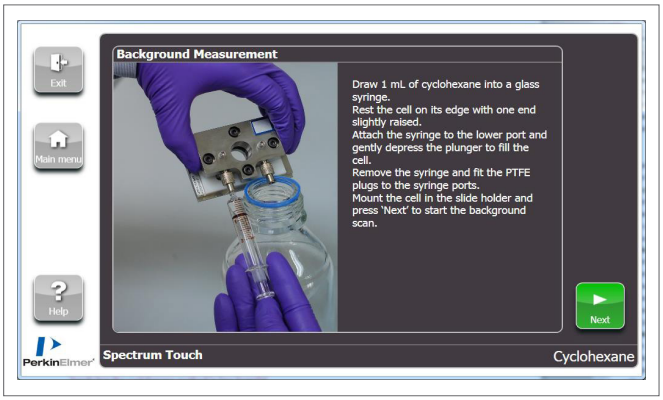

Figure 7. Spectrum Touch method for ASTM D7678.

Conclusion

Quantification of hydrocarbon contamination in water is commonly achieved by Mid-IR spectroscopy as it offers good sensitivity and specificity in comparison with other methods. However, this analysis has also experienced environmental concerns due to the nature of the solvent used. Traditional methods involve use of halogenated solvents and transmission measurements which offer the highest sensitivity, but are expensive and hazardous.

Advancements in technology and enhanced sensitivity of newer FT-IR spectrometers, such as PerkinElmer's Spectrum Two, allows alternative, less harmful methods to be conducted while providing excellent results. Cyclohexane extraction, based on ASTM D7678, is one such method showing good linearity, extraction, and repeatability. Although a weaker absorption band is measured, a useful detection limit sub-ppm is achieved. PerkinElmer's Spectrum Touch software enables quick analysis combined with a simple workflow to acquire results with maximum simplicity and efficiency.

References

1. H. S. Abd El-Gawad. (2014). "Oil and Grease Removal from Industrial Wastewater Using New Utility Approach,". *Advances in Environmental Chemistry.*
2. ASTM D7678-11. (2011). "Standard Test Method for Total Petroleum Hydrocarbons (TPH) in Water and Wastewater with Solvent Extraction using Mid-IR Laser Spectroscopy," *ASTM International.*

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

012499_01 PKI