

# Harnessing the Power of FT-IR to Guarantee Water Safety

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## A global risk to environmental and human health

Pollution of water with oil and grease is a significant risk to human and environmental health; therefore, effective detection and measurement of hydrocarbon contamination is essential. Infrared (IR) spectroscopy has long been a standard method for measuring dispersed oil and grease in process water discharged from offshore oil operations, and has more recently gained application to a wider range of environmental samples and matrices. Contamination incidents creating health and environmental problems can range from major oil spills to small scale domestic disposal.

Large amounts of water are extracted during offshore oil operations, and this must be separated from the oil prior to being discharged back into the sea. However, the separation is not a simple task and recycled water is one of the largest contributors to offshore oil pollution<sup>1</sup>, eventually causing surface contamination and smothering marine life. Long term impacts, including acute toxic effects, can also be caused by specific chemical components of the oil<sup>2</sup>. This potential for harm emphasises the importance of rapid and accurate analytical methods that can be deployed in a variety of environmental testing applications.

Terrestrial sources of pollution are also responsible for a significant fraction of hydrocarbon pollution in coastal waters and sensitive environments like estuaries and wetlands: river and urban runoff sources contribute 20% of petroleum pollution within our oceans<sup>3</sup>. Accordingly, companies that discharge water into rivers or municipal drains are typically required to comply with discharge permits that specify limits of potentially hazardous materials, including hydrocarbons, to ensure that long-term environmental damage is averted. Ideally, this testing can be carried out on-site, ensuring a rapid response to any problems encountered.

Soil is an equally important part of the environment, and is just as vulnerable to pollution. Petroleum pollution can render polluted areas not only unfit for development but also dangerous for nearby communities and ecosystems. Hydrocarbons can easily pass into groundwater, making it unfit for use. If land is to be reclaimed for other uses after decommissioning an oil or gas facility, extensive testing must be carried out to ensure that the soil has not been contaminated. In the event of a spill being discovered, a rapid, portable analysis method can be used to make numerous measurements to accurately delineate the extent of the spill.

### IR testing of water and soil

Although highly effective and well established for the measurement of hydrocarbons in water, historically popular IR methods have raised environmental concerns themselves due to the use of ozone-depleting chlorofluorocarbon (CFC) solvents in the sample extraction process. These environmental concerns have led to the development of a number of alternative approaches to IR analysis of oil pollution, employing less-harmful solvents.

This note explores more environmentally-friendly approaches to the use of IR spectroscopy for detecting and quantifying hydrocarbon contamination. The three methods discussed here are suitable for use across a variety of different applications concerning hydrocarbon contamination.



Figure 1: Sample deposition for the HATR method, constraining the sample to the most brightly illuminated portion of the crystal

### Halogenated solvent extraction

The first of these methods, ASTM D7066, still employs a halogenated solvent, but one that is less damaging to the environment: a mixture of dimers and trimers of chlorotrifluoroethylene. This method employs a traditional long-pathlength measurement of C-H stretching absorptions that not only has the benefit of being standardised and trusted, but also affords excellent sensitivity, with detection limits well below 1 ppm readily obtained<sup>4</sup>. The same methodology can be employed with tetrachloroethylene as the solvent (this is also relatively environmentally safe and widely used for drycleaning and metal degreasing, but has been classed as a probable carcinogen by the EPA<sup>5</sup>). A drawback of the method is the expense involved in obtaining solvents with the very low levels of hydrocarbon residue required in order to avoid interference with the analysis.

### Hexane extraction with IR measurements using attenuated total reflection

Attenuated total reflection (ATR) measurement takes a different approach to transmission IR. Instead of passing light through the sample, it is placed on a crystal through which the light passes by total internal reflection. The evanescent wave created just above the surface of the crystal can be absorbed by the sample, allowing a spectrum to be measured. To apply this technique to measuring oil in water, the sample is extracted with a volatile hydrocarbon solvent, such as hexane. An aliquot of the extract is deposited on the ATR crystal (Figure 1) and the solvent allowed to evaporate, leaving the oil behind. The IR spectrum is then measured, and the oil concentration calculated from the intensity of the absorption (Figure 2).

As well as permitting the use of a cheap, environmentally benign solvent, this method has the major advantage that it enables the measurement of the full IR spectrum of the oil sample, not just the portion visible through the windows in the solvent absorption spectrum. This allows some inferences to be made about the nature of contamination, allowing the identification of particular types of oils or fats that may be present.

A limitation of the ATR method is that it is considerably less sensitive than the previous method (around 10 ppm) and is more time-consuming, due to the evaporation step (requiring around two minutes per sample). Another obvious limitation is that volatile species cannot be included in the measurement, as they will evaporate with the solvent.

### Cyclohexane Transmission

The third method considered here exploits a vibrational mode that is characteristic of hydrocarbons containing  $-CH_3$  groups, and thus is not present in the spectra of cycloalkanes such as cyclohexane (see Figure 3). It thus combines the simplicity of a transmission measurement with the use of a convenient hydrocarbon solvent.

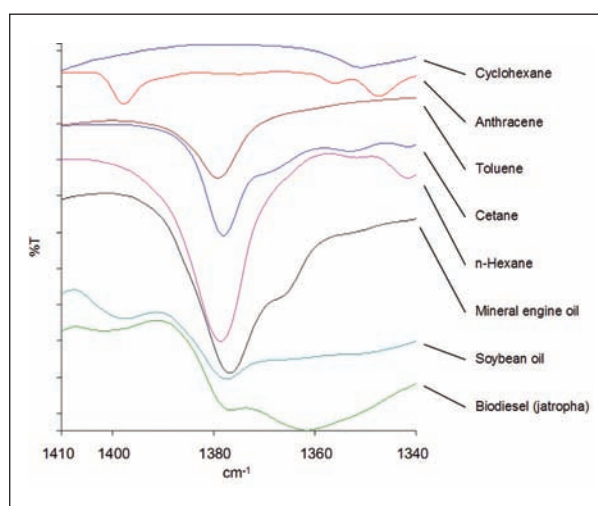


Figure 3: Spectra of a range of hydrocarbons and oils compared with cyclohexane. The spectra are offset for clarity; all have maxima near 100 %T

This method allows rapid measurement with a non-halogenated solvent and can achieve useful sensitivity (around 5 ppm), as demonstrated in Figure 4.

The sensitivity of this method is significantly less than can be obtained with a halogenated solvent, because the band being measured is weaker and the use of cyclohexane necessitates a relatively short pathlength of 0.5 mm. The cyclohexane method shows that it is possible with modern instrumentation, such as the Spectrum Two instrument from PerkinElmer, to obtain an excellent calibration at low concentrations, even with a weak band against an absorbing background (as shown in Figure 3). In applications where sub-parts per million (ppm) detection is not necessary and it is desirable to avoid halogenated solvents, this approach may be ideal.

### Conclusions

Although the use of FT-IR in the determination of oil in water is a classical analytical method, the environmental issues concerning the use of CFCs associated with traditional IR analyses cannot be ignored, and alternative IR methods should be considered, bearing in mind the real sensitivity requirements of the analysis.

Three methods have been considered in this article, and the characteristics of each, including the relative advantages and drawbacks as summarised in Table 1.

Using relatively benign solvents such as tetrachloroethylene or S-316, the traditional long pathlength approach achieved in recent years can be maintained providing sensitivity well below 1 mg/L. If, as in the case for analysis by water companies, it is beneficial to know more about the nature of the contamination, the hexane ATR method can provide this extra information as it allows the user to see the full spectrum of the extracted oil.

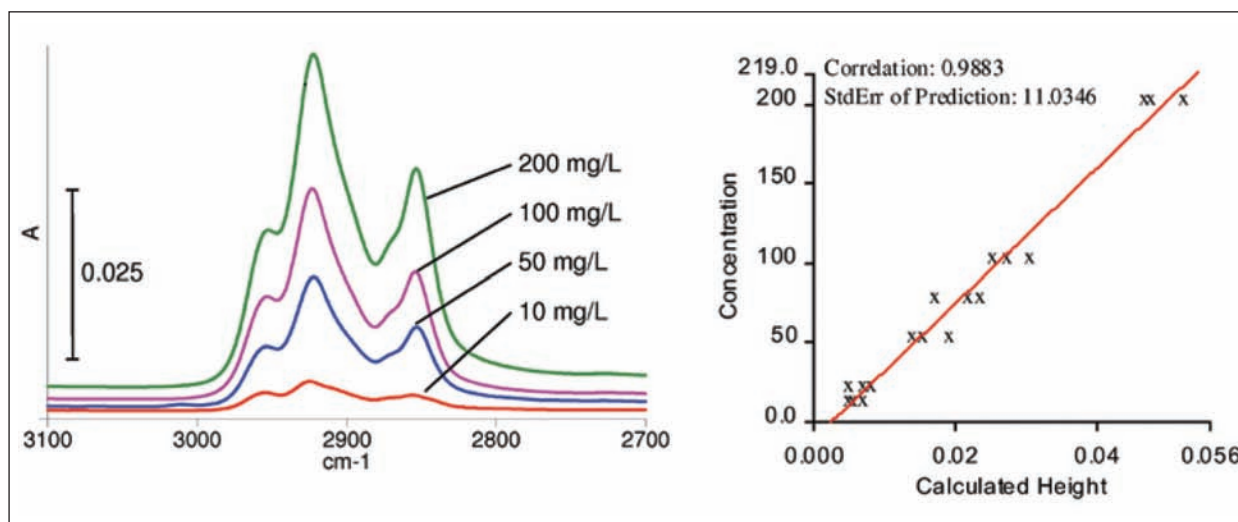


Figure 2: Spectra and calibration curve for the HATR method, measured on a PerkinElmer Spectrum Two FTIR spectrometer. The signal-to-noise ratio is excellent even for the lowest-concentration standard; the primary source of error is variability in the deposition of the sample on the HATR crystal.

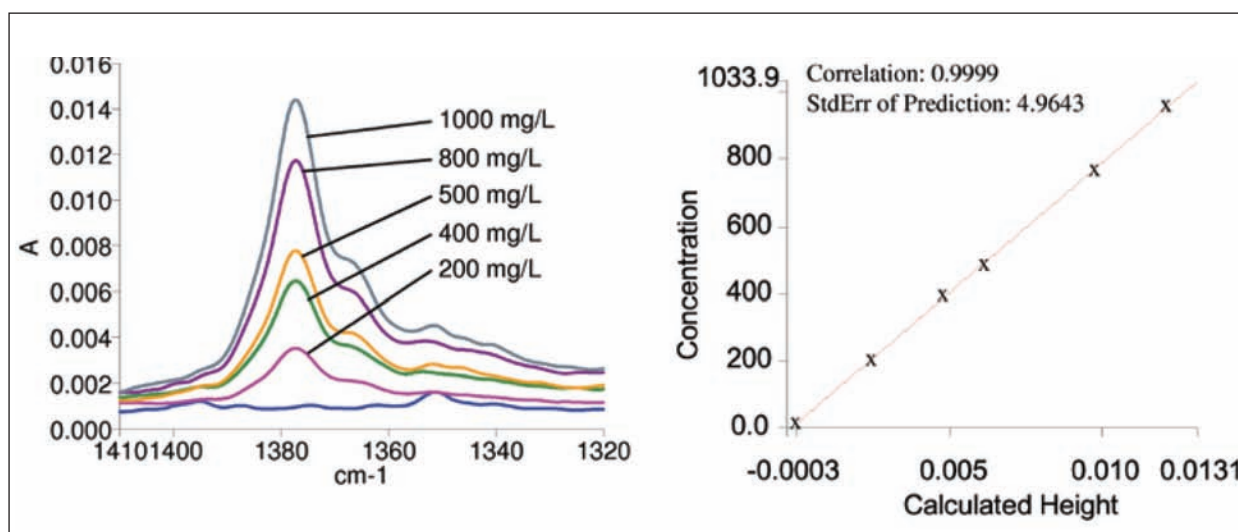


Figure 4: Spectra of paraffin oil in cyclohexane and the calibration graph. Concentrations are specified in mg/L. A PerkinElmer Spectrum Two FTIR spectrometer was used, with a 0.5 mm pathlength liquid cell.

	Tetrachloroethylene or S-316 transmission	Hexane ATR	Cyclohexane transmission
Sample throughput per hour (not including extraction)	15	10	15
Wavenumber range used (cm <sup>-1</sup> )	3200–2700	3200–2700	1410–1340
Calculation details	Max. height in 2945–2915 cm <sup>-1</sup> , baseline points 3100 and 2800 cm <sup>-1</sup>	Max. height in 2945–2915 cm <sup>-1</sup> , baseline 3100 and 2800 cm <sup>-1</sup>	Height at 1377 cm <sup>-1</sup> , baseline at 1396 cm <sup>-1</sup>
Approximate detection limit assuming 5× pre-concentration factor (mg/L in sample)	<0.1	10	5
Advantages	Highest sensitivity		
	Standardised method	Does not require halogenated solvent. Provides full spectrum of extracted oil	Combines rapid measurement with non-halogenated solvent and useful sensitivity
Limitations	Need to find solvent with sufficiently low hydrocarbon residue	Cannot detect volatile species	Less sensitive than halogenated-solvent approach

Table 1: Summary of the three methods for hydrocarbon measurement

The cyclohexane method may offer the best compromise of solvent convenience and speed when maximum sensitivity is not required.

The method comparison presented here illustrates the fact that modern FT-IR instruments, such as the Spectrum Two from PerkinElmer, can achieve very good analytical results even for challenging samples such as minute amounts of oil (~1 mg) deposited on an ATR crystal, or dilute solutions of oil in an absorbing solvent. This capability allows analysts to go beyond the traditional methods for analysing oil contamination of water and soil, and to consider methods using more cost-effective and environmentally benign solvents.

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