

FT-IR Spectroscopy

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Determination of Hydrocarbons in Environmental Samples with Spectrum Two



Introduction

The concentration of dispersed oil and grease in water is an important parameter for human and environmental health. Infrared spectroscopy has long been a standard method for detecting and quantifying hydrocarbon contamination, particularly in water discharged during offshore oil operations.¹

Recently, this analytical technique has enjoyed renewed interest and application to a wider range of environmental samples and matrices, from cooling water, to soil in land reclamation, to drinking water; at the same time, concern over the environmental impact of chlorofluorocarbon solvents has led to the development of a number of alternative approaches using less harmful solvents. This application note presents an overview of three methods and a comparison of their performance:

1. Halogenated solvent extraction and transmission measurement (C–H stretch modes), e.g. ASTM® D7066. This is the traditional approach, but requires the use of relatively expensive solvents that may be harmful.
2. Hexane extraction and ATR measurement allows the use of an inexpensive hydrocarbon solvent, but does not permit the measurement of volatile contaminants.
3. Cyclohexane extraction and transmission measurement (1377 cm^{-1}) exploits a deformation mode that is not present in the spectra of cycloalkanes (see Figure 1), and combines the simplicity of a transmission measurement with a hydrocarbon solvent.²

All three of these methods are supported by the Spectrum Two Environmental Hydrocarbons Analysis System (Figure 2), with the appropriate sampling accessory. This note evaluates the three methods and discusses their relative advantages.

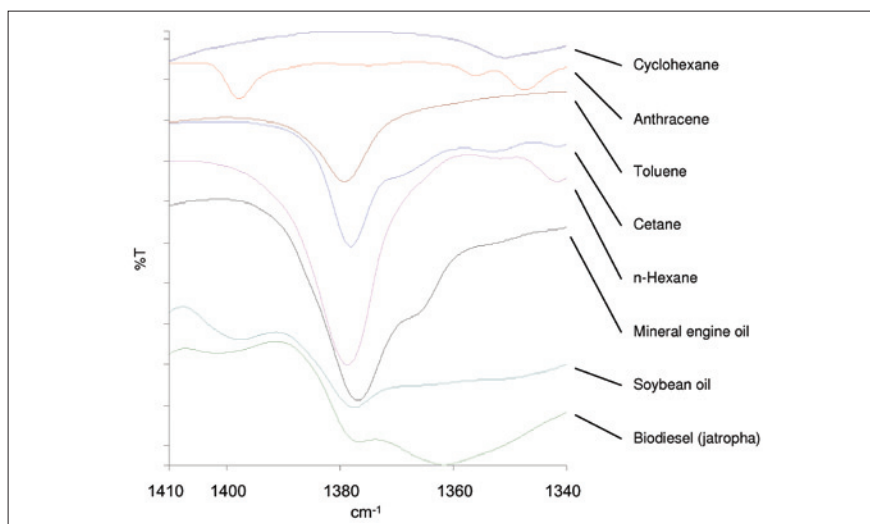


Figure 1. Spectra of some oils and greases compared with cyclohexane.

Extraction with a halogenated solvent: ASTM® D7066

For the ASTM® D7066 method, calibration and spike recovery standards were prepared by diluting a mixture of octanoic acid and isooctane as described in the standard document.³ The solvent specified is dimer/trimer of chlorotrifluoroethylene (CTFE); this was supplied by Bell Quality Lab Supplies (Wyethville, VA).

The spike recovery standards (250 mL) were extracted with three successive 15-mL volumes of CTFE as described in Reference 3. The extract was made up to 50 mL, giving a 5x pre-concentration factor.

The FT-IR spectra of the standards and extracts were measured with a Spectrum Two FT-IR spectrometer using a 10 mm quartz cuvette. The background was measured with the cell full of clean CTFE. An accumulation time of one minute and resolution of 8 cm⁻¹ were used.

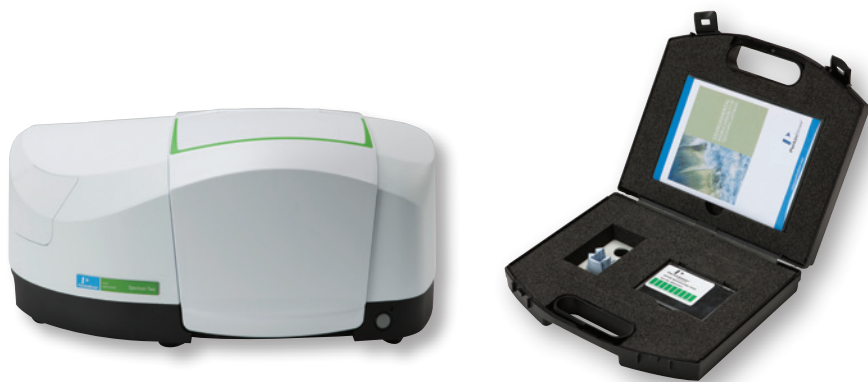


Figure 2. The Spectrum Two Environmental Hydrocarbons Analysis System.

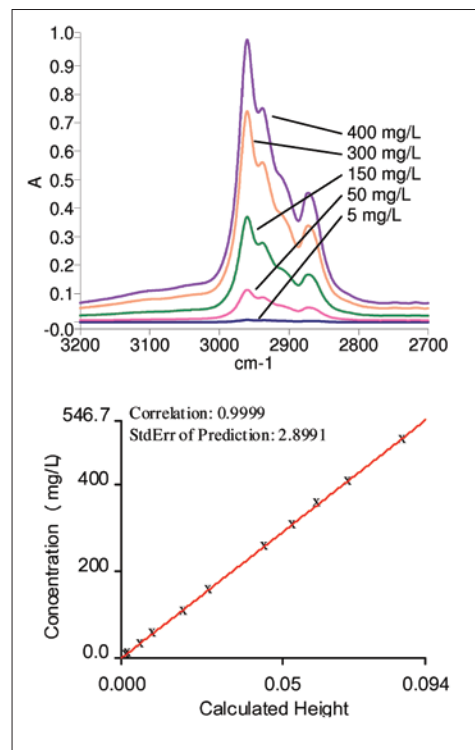


Figure 3. Spectra of oil in CTFE and the calibration graph.

Typical spectra and the calibration curve are shown in Figure 3. The use of a halogenated solvent in the ASTM® D7066 method allows measurement of the strong C–H stretch bands over a very long pathlength, and results in a very low detection limit (LOD). Taking LOD as $5 \times \text{SEP}$ and assuming a $5\times$ pre-concentration factor, the LOD is around 3 mg/L. As the errors include a contribution from standard preparation and are not strictly homoscedastic, a calibration over a lower concentration range would likely result in a smaller LOD.

In fact, if the LOD is calculated as the concentration corresponding to $5\times$ measurement noise, a value of 0.004 mg/L is obtained. This value represents the performance that could be achieved in the absence of standard-preparation errors.

The recovery percentages of the spiked samples are shown in Figure 4. The extraction efficiency varied between 90 and 97% with an average of 94%.

HATR measurement of the evaporated extract

Calibration standards were prepared by diluting weighed amounts of paraffin oil to known volumes with clean pentane.

The spectra were measured on a Spectrum Two FT-IR spectrometer equipped with a PerkinElmer HATR accessory with a 45° ZnSe flat top-plate. The crystal was cleaned by swabbing lightly several times with cotton buds moistened with clean pentane. The background was measured with the clean crystal in place. A 25 μL aliquot of the sample extract was deposited as a row of drops along the centre of the crystal and two minutes allowed for the solvent to evaporate before measuring the sample spectrum (Figure 5).

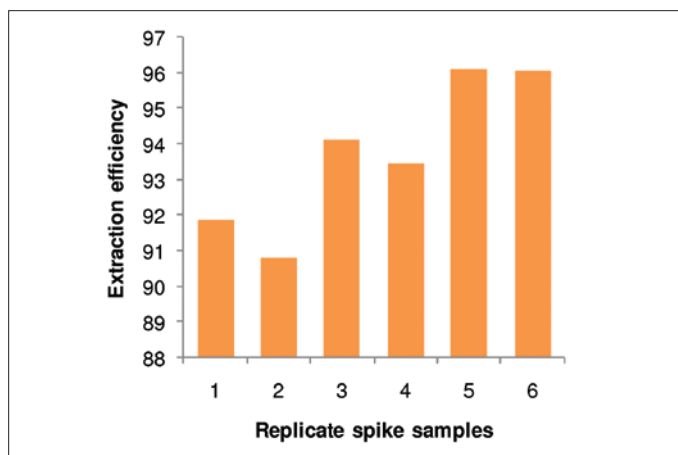


Figure 4. Extraction efficiency for replicate spiked standards.



Figure 5. Sample deposition for the HATR method, constraining the sample to the most brightly illuminated portion of the crystal.

Typical spectra and the calibration graph are shown in Figure 6. By comparison with Figure 3, it can be seen that the absorbance signal for a given concentration is approximately 10× weaker. There is some scatter due to variability in the drying behavior of the sample; in practice, this error may be of a similar order to the variability in the extraction efficiency (Figure 4). Despite these factors, a useful LOD of 11 mg/L is obtained.

An important benefit of the HATR method is that the full spectrum of the oil and grease is obtained, and this allows some inferences to be made about the nature of the contamination. For example, the presence of a band at around 1745 cm⁻¹ would indicate that esters – such as triglycerides from animal fats or vegetable oils – are present in the sample.

Transmission measurement with cyclohexane solvent

Calibration standards were prepared by diluting weighed amounts of paraffin oil to known volumes with clean solvent.

The IR spectra were measured in a liquid cell with CaF₂ windows and a pathlength of 0.5 mm, chosen to give the optimum transmittance of the solvent blank (~33%) at the analytical wavelength of 1377 cm⁻¹. The sample spectrum was ratioed against a background of clean solvent. Typical spectra and the calibration graph are shown in Figure 7.

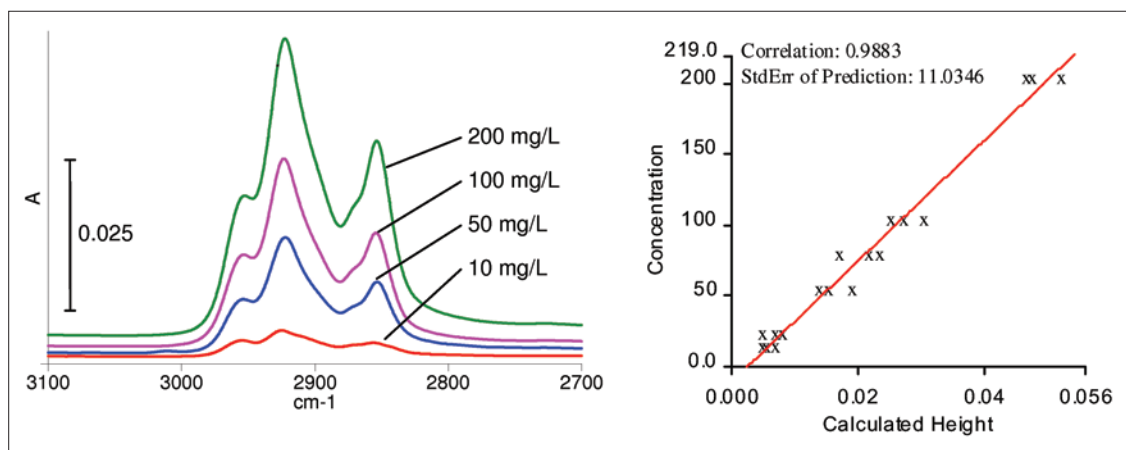


Figure 6. HATR spectra of evaporated samples and the calibration graph. Concentrations are specified in mg/L.

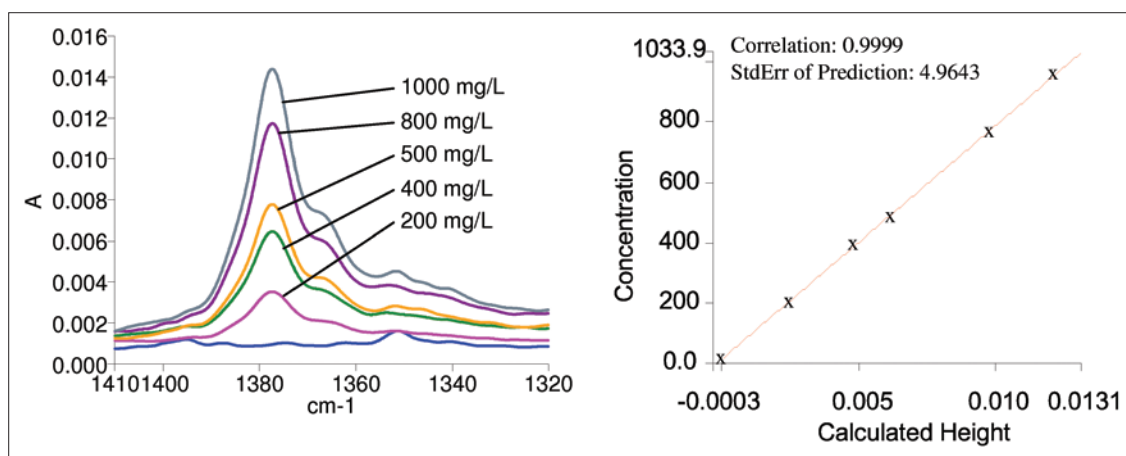


Figure 7. Spectra of paraffin oil in cyclohexane and the calibration graph. Concentrations are specified in mg/L.

These cyclohexane results illustrate that, with the Spectrum Two instrument, it is possible to obtain an excellent calibration at low concentrations even with a weak band against an absorbing background. An LOD of 5 mg/L can easily be obtained. While this is similar to the calculated LOD for the ASTM® D7066 method, the achievable detection limit with a halogenated solvent is much better because the available signal (including both extinction coefficient and pathlength advantages) is approximately 250 times greater.

Application to soil samples

The extraction process for soil is significantly more difficult, particularly if the soil is wet. Techniques such as Soxhlet extraction or sonication can help achieve high extraction efficiency. If the soil sample can be dried and finely ground, shaking with solvent for a few minutes may be sufficient.

Spiked soil samples (100, 200 and 400 mg/kg) were prepared by dissolving paraffin oil in hexane and dispersing a known volume over a known mass of dried, finely ground soil, then allowing 1 hr for the solvent to evaporate. Samples of 10 g were extracted with 15 mL hexane by shaking in HPLC vials for 5 minutes. Portions of the solvent layer were withdrawn and filtered through 25 µm syringe filters before analysis with the HATR method described above.

The results are shown in Figure 8. From this plot we can conclude that there is a significant concentration of extractable hydrocarbons present in the “blank” soil sample, around 50 mg/kg. Subtracting this offset results in good agreement for the 100 and 200 mg/kg samples. The result for the 400 mg/kg sample is somewhat too low, indicating that this may be exceeding the linear range of the calibration.

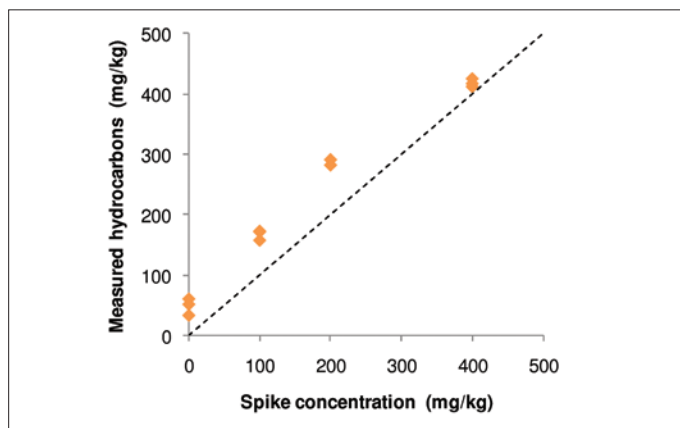


Figure 8. Analysis of spiked soil samples. The dashed line has intercept zero and slope one.

Conclusions

The determination of oil in water by FT-IR is a classical analytical method that in recent years has suffered from concerns and restrictions around the environmental safety of the solvents typically used. However, there are a number of approaches to ensure the method remains viable. The traditional long-pathlength approach can be maintained by using relatively benign solvents such as tetrachloroethylene (although this has been classed as a probable carcinogen by the EPA4) or S-316, and can provide sensitivity well below 1 mg/L.

The sensitivity of modern instruments such as the Spectrum Two is such that alternative sampling methods can provide excellent performance. Deposition of the extract onto an ATR crystal and evaporation of the solvent has the important advantage of allowing the entire spectrum of the oil to be measured, not just the portion visible through the solvent absorption window. However, any volatile components of the contamination will be lost.

A third method is to use cyclohexane as the extraction solvent. This necessitates a relatively short pathlength (0.5 mm) and the measurement of a weaker band, leading to poorer sensitivity than is achievable with a halogenated solvent. However, for applications where sub-ppm detection is not necessary and it is desirable to avoid halogenated solvents, this approach may be ideal.

Table 1. Summary of the three methods for hydrocarbon measurement.

	Tetrachloroethylene or S-316 transmission	Hexane ATR	Cyclohexane transmission
Sample throughput per hour (not including extraction)	15	10	15
Wavenumber range used (cm ⁻¹)	3200-2700	3200-2700	1410-1340
Calculation details	Max. height in 2945-2915 cm ⁻¹ , baseline points 3100 and 2800 cm ⁻¹	Max height in 2945-2915 cm ⁻¹ , baseline 3100 and 2800 cm ⁻¹	Height at 1377 cm ⁻¹ , baseline at 1396 cm ⁻¹
Approximate detection limit assuming 5x pre-concentration factor (mg/L in sample)	<0.1	10	5
Advantages	Highest sensitivity. Standardized 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 2. Ordering information. The below Analysis Packs will equip your Spectrum Two instrument with the appropriate sampling accessory and dedicated Spectrum Touch software for environmental hydrocarbons analysis.

L1608006	Environmental Hydrocarbon FT-IR ASTM® D7066 Analysis Pack
L1608008	Environmental Hydrocarbon HATR FT-IR Analysis Pack
L1608007	Environmental Hydrocarbon FT-IR Cyclohexane Analysis Pack

References

1. UK National Engineering Laboratory, 2005. Oil-In-Water Analysis Method (OIWAM) JIP Final Report. Available online: https://www.og.decc.gov.uk/environment/NEL-Oilin_Water_Analysis_Method_%28OIWAM%29_-_Final_Report.pdf (accessed 20 January 2011).
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3. ASTM® International, 2004. D7066 - 04e1 Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination
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