

FT-IR Spectroscopy

Author:

Ian Robertson

PerkinElmer, Inc.

Seer Green, England



ASTM D-7575. A Rapid, Green, FT-IR Method for Testing Hydrocarbon Contamination in Environmental Water Samples

Introduction

Historically, Infrared (IR) Spectroscopy methods were widely used for quantifying oil, grease, and hydrocarbons in water samples. IR spectroscopy allows for fast and easy measurement of

these types of samples. Various IR methods were used globally according to local regulations or protocols. Prior to the Montreal Protocol in 1989, prohibiting the use of chlorinated solvents, most of the IR methods involved the extraction of hydrocarbons in water samples used carbon tetrachloride, CCl_4 , as the extraction solvent. Alternative methods were required to replace these methods, with many laboratories moving away from IR methods. Some of these methods, such as EPA 1664, still use hazardous solvents for the extraction of hydrocarbons from water samples prior to gravimetric measurement.

This Application Note describes a new solvent-free IR method, ASTM D-7575, that uses an IR-transmitting membrane material that will extract and retain the hydrocarbon species as a known quantity of water sample is passed through it.

The ASTM D-7575 method makes use of ClearShot Extraction Technology^{®1}, Figure 1a, based on an IR amenable solid phase extraction membrane. The water sample to be analysed is passed through the disposable extractor device that will retain any oil or grease within the sample, followed by IR transmission analysis on the Spectrum Two™ FT-IR, as in Figure 1b, to determine the amount of oil or grease present in the original sample.

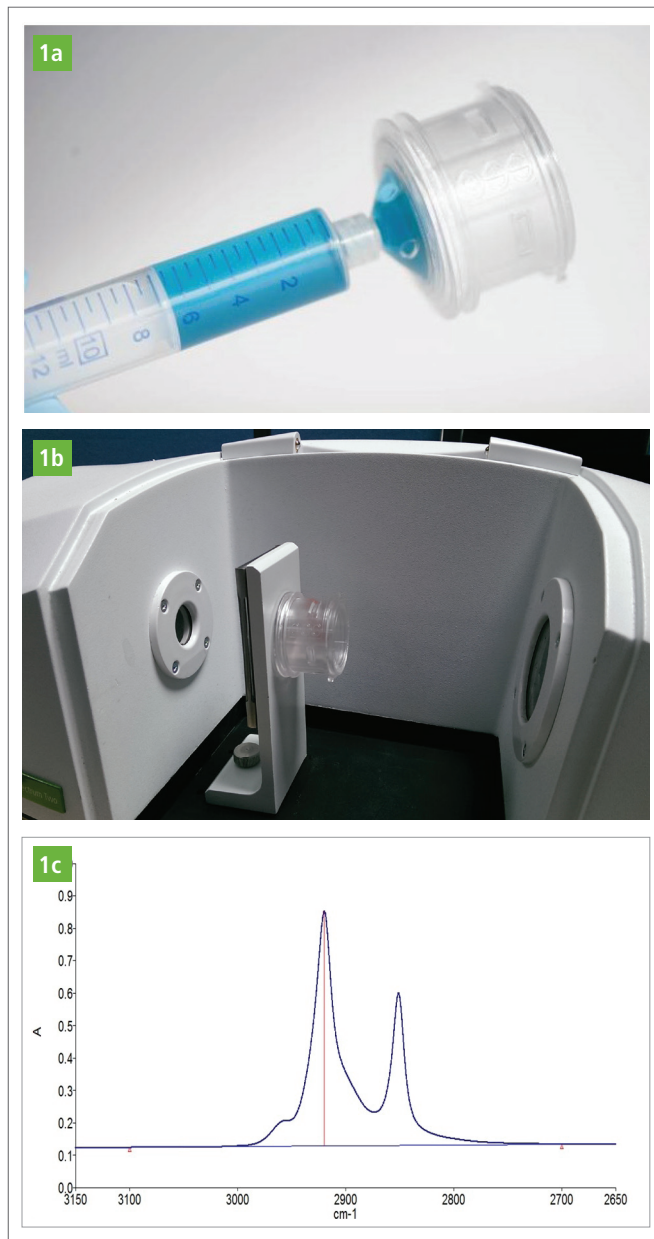


Figure 1. Analysis overview. (a) Syringe an accurate amount of sample through the ClearShot extractor. (b) Dry the extractor and place in the extraction device sample holder in the FT-IR. (c) Scan the sample and quantify the hydrocarbon content based on the hydrocarbon intensity at 2920 cm⁻¹.

The IR spectrum of an extractor device ratioed against the extractor sample holder is shown as Figure 2. It is clear from this spectrum that there is a considerable range of the IR spectrum that can be used for the analysis, not just the hydrocarbon region around 2920 cm⁻¹.

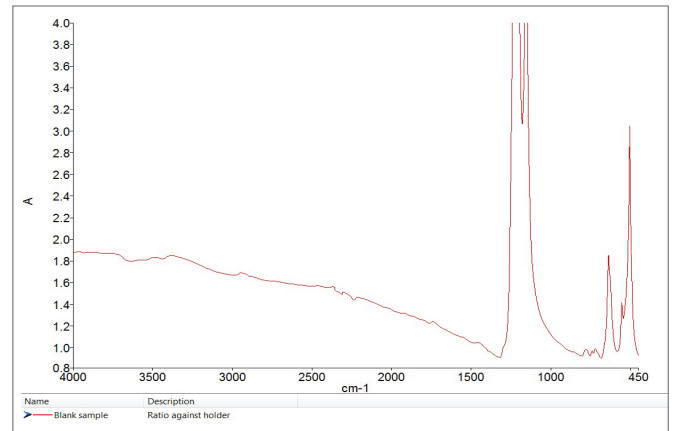


Figure 2. IR spectrum of unused extractor device.

Calibration Process

Calibration of the system for hydrocarbon concentration is required prior to sample analysis. A range of solid state Calibration Standard Devices (CSD) is provided containing known amounts of hydrocarbon. A background spectrum is recorded using a blank extractor device. The spectra of the CSDs are then run and these spectra are used for the calibration in the Spectrum Quant™ software using a Beer's Law algorithm based on the peak height of the absorbance spectrum at 2920 cm⁻¹. The spectra obtained from the CSDs are shown as Figure 3, with the calibration line shown as Figure 4. CSD 5 was omitted from the calibration and used as a validation test sample.

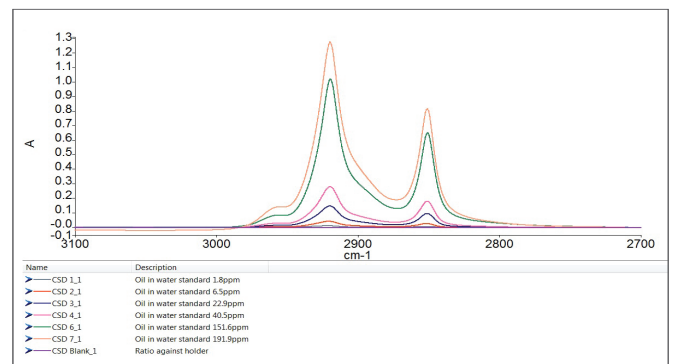


Figure 3. Spectra obtained from the set of CSDs.

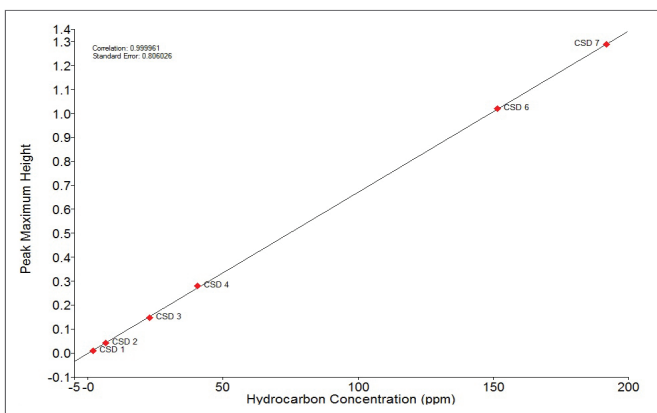


Figure 4. Beer's Law Calibration for the CSDs.

The calibration had an excellent correlation value of 0.999961.

Procedure for Sample Analysis

Water samples to be analysed are typically acidified to a pH of <2 and kept refrigerated if the sample is not going to be measured immediately. Prior to extraction the sample should be allowed to reach room temperature and requires homogenization. In some cases homogenization can be achieved by vigorous shaking of the sample bottle. If not, then the sample should be homogenised in an ultrasonic bath for up to 20 minutes at 40 °C. The sampling method for ASTM D-7575 uses a Luer syringe to sample 10 mL of the homogenized water sample. The syringe is connected using the Luer connection to the extractor device and the 10 mL of sample is passed through the (vertically held) extractor. For best accuracy the syringing of the sample should be performed using a syringe pump that will accurately dispense the required amount of sample. Once the 10 mL of sample have been syringed into the extractor device the extractor is inverted to remove the bulk of the sampled water. The extractor device is then connected to a drying manifold that uses a dry, oil-free supply of compressed air to completely dry the device. A typical drying time is approximately 10 minutes, although to maximize sample throughput multiple extractor devices can be simultaneously dried on the drying manifold. Once dried the extractor device is ready for analysis.

The background spectrum on the Spectrum Two FT-IR is collected on a clean extractor device in the transmission sample holder, Figure 5, using 200 scans at 8 cm⁻¹ resolution.



Figure 5. ClearShot extractor in Spectrum Two.

The processed sample extractor device is then placed in the sample holder and the absorbance spectrum measured using 50 scans. The hydrocarbon content for the sample is then predicted using the calibration line from the Calibration Standard Devices.

Method Validation

Calibration Standard Device #5 was omitted from the calibration and used as a sample to validate the method. Repeat measurements were performed on this sample to determine the repeatability of the results by running: (a) repeat measurements without removing the sample and (b) repeat measurements after removing and replacing the sample. The results are shown as Table 1.

Table 1. Repeatability measurements on CSD 5.

Sampling Technique	Number of Measurements	Mean Hydrocarbon Content (ppm)	Standard Deviation (ppm)
(a) Repeats	12	107.577	0.1355
(b) Replace and repeat	10	106.952	0.997084

The spectra obtained from the repeat measurements are shown in Figure 6.

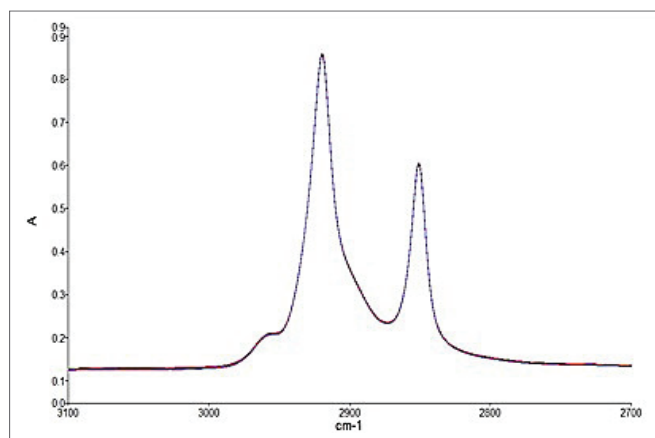


Figure 6. Overlaid spectra of repeat measurements on CSD5.

The measurements are seen to be very reproducible with a slight degradation observed when the sample is removed and replaced.

Measurement of Effluent Samples

A series of samples were collected from an industrial effluent stream for analysis by the described method. After sample processing, the spectra of the samples were measured and the hydrocarbon content calculated. The data collection and analysis were performed using a Spectrum Touch™ method specifically designed to perform this hydrocarbon analysis. The method is designed for routine operators, and guides the user through the analysis with on-screen instructions. An example screen is shown as Figure 7.

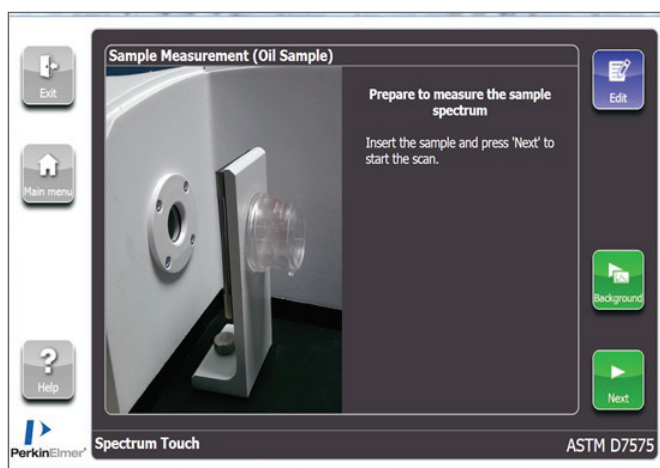


Figure 7. Spectrum Touch method for ASTM D-7575.

The spectra obtained from the samples are shown overlaid in Figure 8 with the calculated hydrocarbon content shown in Table 2.

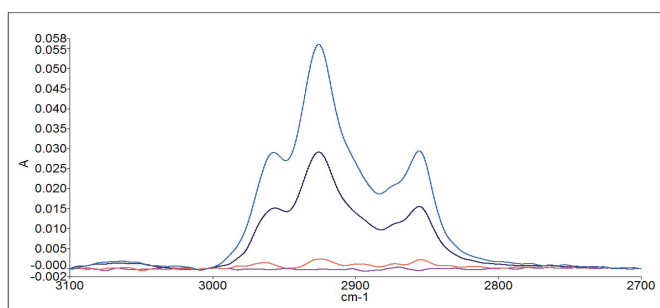


Figure 8. Effluent samples spectra.

Table 2. Effluent samples results

Sample Name	Method Name	Hydrocarbon Concentration (ppm)
Blank_1	ASTM D-7575	-0.057
Sample A	ASTM D-7575	7.41
Sample B	ASTM D-7575	3.61
Sample C	ASTM D-7575	0.065

Summary

The ASTM D-7575 method described is a fast and easy alternative to the existing oil in water methods and also has several advantages:

- Economical
- Solvent-free
- High Sample Throughput
- Adheres to EPA Green Principles
- Rapid calibration with solid state standards
- Easy implementation
- Produces equivalent result to EPA 1664 (Data available on request)

In addition, the Spectrum Two is a portable instrument that can be taken to the site where the samples need to be measured.

Method Specifications

Detection Limit < 1 ppm

Lower quantification < 5 ppm

Linear reporting range 5 – 200 ppm

Time required per sample*: 15 minutes

*Parallel sample processing allows a single operator to perform up to 20 measurements per hour

Reference

1. Clearshot Extraction Technology is a registered trademark of Orono Spectral Solutions, Inc. , Bangor, ME 04401