

Measurement of Dispersed Oil in Water Using an Infrared Analysis Method

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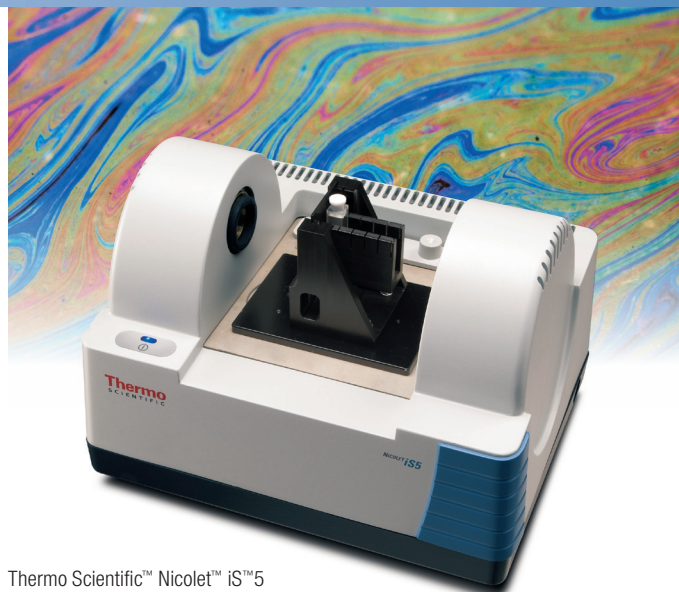
Key Words

FT-IR, Total Petroleum Hydrocarbons (TPH), Oil in Water (OIW), Recoverable Oil and Grease and Nonpolar Material

Introduction

The environmental and health issues associated with polluted water supplies are of growing worldwide concern. Population growth, industrial expansion, and intensive agricultural practices are major contributors to increasing pollution levels in surface and ground waters as well as the planet's oceans. Of particular alarm is the increase in hydrocarbons due to industrial runoff. Industrial run-off is a major contributor to hydrocarbon pollution of waterways that can be traced to oils, lubricants, fuels, or sludge by-products produced by point-source industrial plants. Additionally, more diffuse sources of hydrocarbon pollution from roadways and agricultural sites continue to degrade water quality. In order to trace, control, and prevent hydrocarbon pollution in our waterways, government and industry agencies are looking to inexpensive, reliable, and rapid methods to test water samples.

Infrared spectroscopy has long been one of the preferred analytical techniques to determine hydrocarbon levels in the environment. The materials of interest can be classified as total petroleum hydrocarbons (TPH), gasoline range organics (GRO), oil and grease (OG), or simply oil in water (OIW). Traditionally, a water or soil sample was extracted with a halogenated solvent that contained no C-H bonds and the magnitude of the hydrocarbon peak (C-H) was analyzed in a long path liquid cell with infrared transparent windows. The most common solvents employed were carbon tetrachloride and certain Freons. Liquid extraction with halogenated solvents for analysis with FT-IR is the basis of many government and industry methods worldwide, including many European and Asian countries. Furthermore, the United States Environmental Protection Agency (US EPA) created several methods based on liquid extraction in the 1980's that were successfully employed to monitor hydrocarbon pollution.



Thermo Scientific™ Nicolet™ iS™5
FT-IR spectrometer configured with cuvette
holder and 10 mm cell

While these halogenated solvents were considered relatively non-toxic and non-flammable, they were identified as a major source of ozone-depleting chemicals and were detectable in the upper atmosphere. In 1987, the Montreal Protocol, an international environmental agreement, established requirements that began the worldwide termination of ozone-depleting CFCs (chlorofluorocarbons). While the use of CFCs as an analytical solvent has drastically decreased, they are still employed in various parts of the world, and their production will not be completely eliminated for years to come. Due to the convenience of the infrared (IR) method, several groups have developed alternative techniques that do not employ these prohibited solvents.

The American Society for Testing and Materials (ASTM) released an IR method in 2004, method D7066-4, that employed an oligomer of chlorotrifluoroethylene. In Europe the UK Department of Energy and Climate Change (DECC) issued “*Guidance Notes for The Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges*” based on the Offshore Petroleum Activities (Oil Pollution Prevention and Control) Regulations of 2005 and revised in 2010. While the primary analytical method for oil in water is based on gas chromatography, the DECC has proposed that an IR method based on hydrocarbon extraction with tetrachloroethylene is an acceptable secondary method for off-shore oil facilities. In this guideline, they provide detailed instructions on two different IR methods. The first method, similar to the ASTM method, is based on a single peak measurement at 2930 cm^{-1} which corresponds to the amount of $-\text{CH}_2$ present in the sample. A second method, more useful for samples containing aromatic hydrocarbons, is the triple peak method, which measures the intensity at three spectral regions: 2930 cm^{-1} $-\text{CH}_2$, 2960 cm^{-1} $-\text{CH}_3$ and 3030 cm^{-1} Ar-CH. This method is modified from method IP 426:98 (04). Similar methods using halogenated solvent extraction and multiple peaks analysis have been approved by numerous countries including China, Germany, India, France, and the UK.

In this paper, we report on experiments designed to verify the performance of a Thermo Scientific Nicolet iS5 FT-IR spectrometer for measuring hydrocarbon content in water samples. While our work is easily adapted to other liquid/liquid extraction methods worldwide, it is based on the single-peak DECC Infrared/Tetrachloroethylene Method and ASTM D7066-4 method using tetrachloroethylene as the extraction solvent. Based on calibration samples produced from mixtures of iso-octane and octanoic acid as defined in the ASTM method, we determined a Root Mean Square Error of Prediction (RMSEP) of less than 0.001 mg/mL for validation samples. This corresponds to less than 1 ppm for a 50 mL extraction from 900 mL water.

Experimental Methods

With the exception of using tetrachloroethylene instead of the more expensive proprietary solvent, this work closely follows the procedure described in the ASTM D7066-4 method. The equipment required for the ASTM method is listed below.

Materials

All glassware that came in contact with the sample was rinsed with tetrachloroethylene prior to beginning this procedure. Reagent grade chemicals were selected for this analysis method. Tetrachloroethylene was free from hydrocarbon contamination.

- **Infrared Spectrometer**, Nicolet iS5 FT-IR spectrometer. Alternatively, any FT-IR spectrometer (e.g., Thermo Scientific Nicolet iS10 spectrometer) capable of making measurements at 2930 cm^{-1} can be used.
- **IR-suitable Cell(s)**, Infracil quartz, 10 mm path length or longer for lower concentrations
- **Glass Funnel and Filter Paper**, 11 cm ashless
- **Glass Graduated Cylinder**, 100 mL
- **Glass Separatory-Funnel**, 500 mL , with fluoropolymer stopcock and stopper
- **Volumetric Flasks**, glass, various ($10, 25, 50, 100,$ and 200 mL)
- **Micropipette or Volumetric Pipettes**, glass, various ($0.50, 1.00, 5.00, 10.0$ and 25.0 mL)
- **Analytical Balance**
- **Syringes**, 50 and 500 mL
- **Isooctane (2, 2, 4-trimethylpentane)**, 98% minimum purity, for use in calibration
- **Octanoic acid**, 98% minimum purity for use in calibration
- **Silica Gel**, Anhydrous. Dry at $200\text{--}250\text{ }^\circ\text{C}$ for 24 hours minimum and store in a desiccator or tightly sealed container.
- **Sodium Sulfate (Na_2SO_4)**, ACS, granular anhydrous. Dry at $200\text{--}250\text{ }^\circ\text{C}$ for 24 hours minimum and store in a tightly sealed container until use.
- **Tetrachloroethylene**, ACS Spectroscopy Grade
- **Hydrochloric acid**, ACS, $1 + 1$. Mix equal volumes of concentrated HCl and water

Calibration and Sensitivity

Initial calibration standards were prepared from equal weights of iso-octane and octanoic acid to cover a concentration range from 0.5 mg/mL to 0.025 mg/mL total hydrocarbon in tetrachloroethylene. Spectra were acquired from the standard solutions in a 10 mm path length cell in a Nicolet iS5 spectrometer. Each measurement takes less than one minute at 8 cm⁻¹ resolution. A reference spectrum from the pure solvent was subtracted from each standard. The results of these measurements are shown in Figure 1 along with the results of a peak-height Beer's Law method developed using the Thermo Scientific™ OMNIC™ TQ Analyst™ software. The Root Mean Standard Error of Calibration (RMSEC) for this method was found to be approximately 0.003 mg/mL.

A second set of more dilute standards were prepared from the same stock solution to cover the concentration range from 0.0025 mg/mL to 0.05 mg/mL. The spectra and calibration results are shown in Figure 2.

Water Extraction Reproducibility

Two important variables in determining limits of detection are 1) the amount of initial water sample extracted and 2) the amount of oil recovered from the sample. The following was reported by Thermo Scientific Applications Laboratory (Milan, Italy) showing the results of a recovery experiment for very low levels of hydrocarbon-spiked samples. Water samples were prepared by mixing two liters with 39.6 µg of hexadecane/iso-octane reference to a final concentration of 19.80 µg/L. The seven replicate samples were acidified with HCl to a pH <2 before extraction with tetrachloroethylene. Each water sample was extracted twice with 20 mL aliquots of tetrachloroethylene. Both extracts were then passed over a bed of Florisil that was washed with a small volume of tetrachloroethylene, bringing the final combined volume up to 50 mL for each sample processed. The extracts were analyzed with the FT-IR spectrometer and peak heights at 2930 cm⁻¹ measured. The results were compared to the prepared standards, and the sample concentrations calculated using Thermo Scientific OMNIC software. The results from seven replicates are shown in the Table 1. Average recovery was calculated to be 19.14 ± 1.50 µg/L.

Sample	Calculated Recovery (µg/L)	Deviation (from 19.80 µg/L)
1	17.00	-2.80
2	18.25	-1.55
3	20.50	0.70
4	18.50	-1.30
5	19.50	-0.30
6	18.75	-1.05
7	21.50	1.70
ave	19.14	-0.66
std dev	1.50	1.50

Table 1: Hydrocarbon recovery as measured by FT-IR spectroscopy. Sample recovery was calculated, and the deviation from the target (19.80 µg/L) determined.

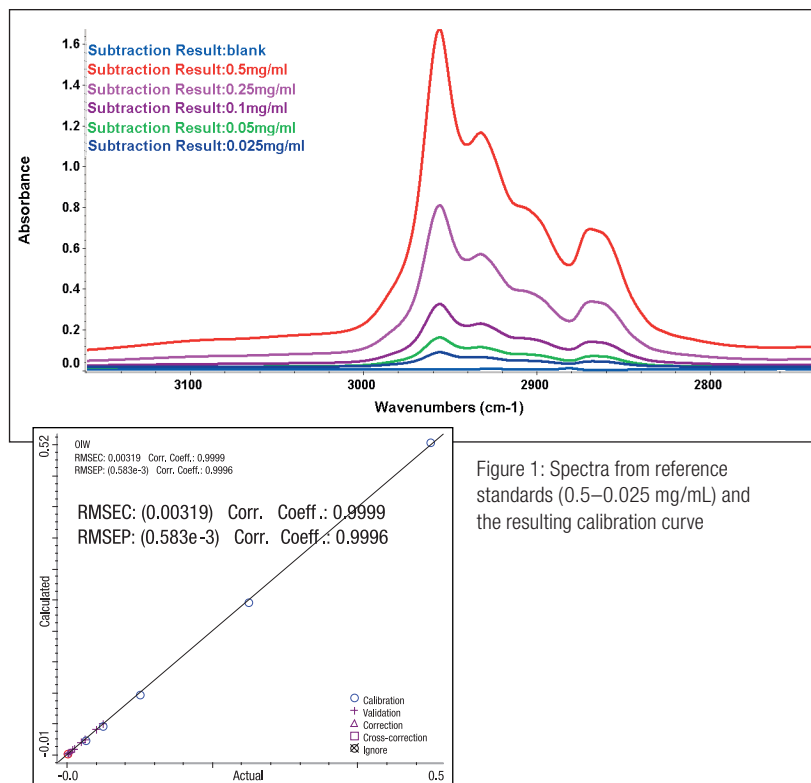


Figure 1: Spectra from reference standards (0.5–0.025 mg/mL) and the resulting calibration curve

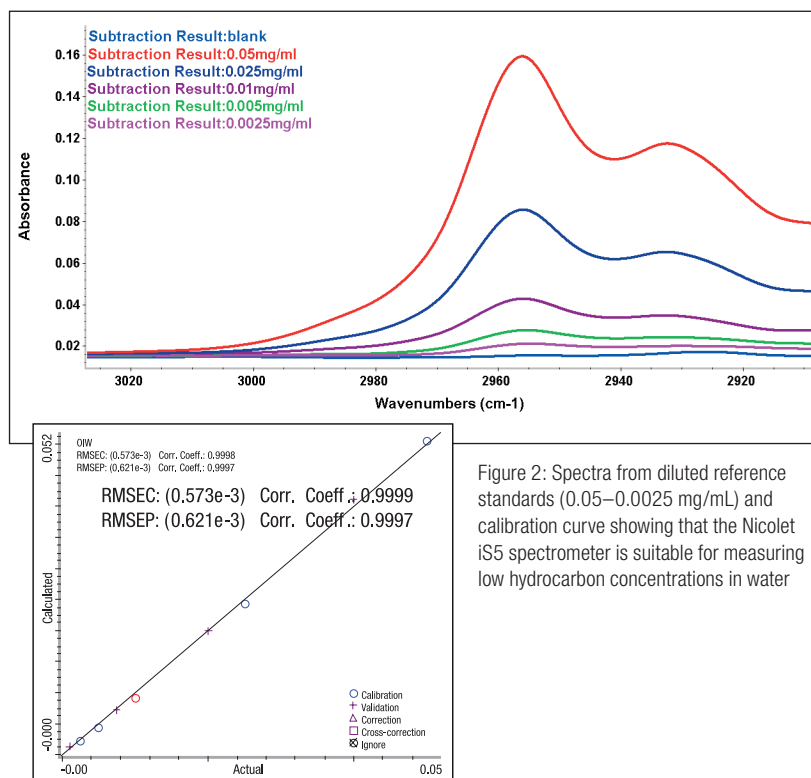


Figure 2: Spectra from diluted reference standards (0.05–0.0025 mg/mL) and calibration curve showing that the Nicolet iS5 spectrometer is suitable for measuring low hydrocarbon concentrations in water

Conclusions

Our goal in this investigation was to evaluate the capabilities of the Nicolet iS5 FT-IR spectrometer to rapidly measure hydrocarbon levels in water or soil samples using a CFC-free extraction method based on ASTM D7066-4. We successfully demonstrated that the instrument is capable of 10-fold higher sensitivity than that described in the ASTM method. Similar values for RMSEC and RMSEP support the robustness of the Beer's Law method and the Nicolet iS5 spectrometer for measuring low levels of hydrocarbons in water. We were also able to show the reproducibility of this extraction method to quantify hydrocarbons in spiked water samples. With today's modern computerized instruments and multivariate statistical analysis techniques, more sophisticated algorithms can be applied to validate quantitative methods, including multiple linear regression, partial least squares, or simply using single or multiple peak measurement methods.

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