

Low-Level Measurement of Oil and Grease in Water Using Solvent-Free Infrared Analysis Method ASTM D7575

Mike Garry, Ron Rubinovitz, Thermo Fisher Scientific, Madison, WI, USA

Luke Doucette, Dean Smith, Tom Schwarz, Orono Spectral Solutions, Inc. (OSS, Inc.), Bangor, ME USA

Key Words

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Introduction

Water quality testing is of great importance to address environmental and health concerns. A critical component being analyzed is hydrocarbons resulting from oil and grease contamination. In fact, the oil and grease component is one of the five conventional pollutants designated in the 1974 Clean Water Act.¹ The measurement of oil and grease is included in all National Pollution Discharge Elimination System (NPDES) permits, pre-treatment permits, and Industrial Effluent Guidelines.² Oil and grease is the second most enforced pollutant; superseded only by pH.

Prior to the Montreal Protocol, which is an international treaty designed to phase out substances responsible for ozone depletion, infrared spectroscopy was used as a standard and reliable method for measuring the hydrocarbon content in water.³ Oil and grease were extracted from water samples using Freon®, a chlorofluorocarbon (CFC) solvent that contains no hydrocarbon (C-H) bonds, and an infrared spectrum of the resulting extract was measured using a long pathlength liquid cell. Once the Montreal Protocol went into effect in 1989, the EPA abandoned the Freon extraction infrared method in favor of an *n*-hexane extraction mass determination method (EPA 1664).⁴ Although this eliminated the use of CFC solvents, it created four new issues:

1. Safety concerns because a flammable liquid is required, necessitating the use of explosion-proof hoods and other protective devices;
2. Health concerns since *n*-hexane is a known neurotoxin and is potentially harmful to fertility;
3. Environmental concerns since an estimated 1.1 million liters of *n*-hexane used for EPA Method 1664A analyses must be purchased and then disposed of each year⁵; and
4. A significant increase in analysis time.



Figure 1:
Thermo Scientific™
Nicolet™ iS™5 FT-IR
spectrometer

The shortcomings of the *n*-hexane extraction gravimetric method are now addressed by a validated method for hydrocarbon determination: “ASTM D7575 – Standard Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination” which is described in this document.⁶ In this method, a fixed volume of homogenized sample is passed through a disposable proprietary membrane that traps and concentrates the hydrocarbons. After a short drying time, an infrared transmission spectrum of the membrane is collected and the peak height at 2920 cm⁻¹ (hydrocarbon stretching mode) is applied to a calibration equation to report the concentration of total oil and grease in the original sample. This “green” method offers several advantages including eliminating the use of solvents, shortening the analysis time and reducing costs.

Experimental

The procedure described in this section closely follows the ASTM D7575 standard test method. The equipment required is listed below.

Materials

- **Infrared Spectrometer** – Such as the Thermo Scientific Nicolet iS5 FT-IR spectrometer (Figure 1)
- **Sample Bottles** – 1 L glass
- **Ultrasonic Bath** – Capable of heating to 40 °C and holding 1 L sample bottle(s)
- **10 mL Syringes** – Glass or plastic, oil free
- **Syringe Pump** – Capable of holding 10 mL syringe
- **Volumetric Pipettes** – 10 mL and 1 mL
- **Volumetric Flask** – 1 L

Items available only from OSS, Inc.⁷

- **ClearShot™ Extraction Technology cartridges** – Contains proprietary oil and grease extraction membrane in a polymer housing with Luer-lock connectors (Figure 2)
- **ClearShot Holding Card** – Holds ClearShot extraction cartridge in place for infrared measurement (Figure 2)
- **Calibration Standard Devices (CSD) Set** – Seven preloaded ClearShot extraction cartridges with certified oil and grease levels plus a “blank”
- **Drying System** – Variety of configurations available to push dry air through Extractor cartridges



Figure 2: ClearShot Extraction package

Reagents and Standards

- **Laboratory Reagent Water** – Deionized
- **Hydrochloric Acid** – 12.1 M
- **Acetone** – ACS, residue less than 1 mg/L
- **Hexadecane** – 98% purity or above
- **Stearic Acid** – 98% purity or above

Sample Analysis

Below is a brief description of the sample analysis steps used to complete ASTM D7575. Specific details can be obtained by reviewing the ASTM D7575 Standard Test Method or the OSS Standard Operating Procedure for ASTM D7575.^{6,8}

Sample Collection

Samples are collected into cleaned glass containers and acidified with hydrochloric acid to a pH of 2 in order to assure stability.

Sample Homogenization

Just prior to sample processing, the samples are homogenized in collection bottles by placing them in an ultrasonic bath heated to 40 °C for 20 minutes.

Sample Processing

Ten milliliter syringes are overfilled with about 12 mL of sample (Figure 3). Bubbles are removed leaving slightly more than 10 mL of sample in the syringe. The ClearShot extractor is attached to the syringe pump programmed to deliver 10 mL of sample through the membrane (Figure 4). The extractor loaded with sample is dried for a few minutes by attaching the cartridge to a source of oil-free compressed air (Figure 5).

Instrumental Analysis

The infrared transmission spectrum of an unused extractor is measured by attaching it to a ClearShot Holder Card to provide a background scan (Figure 6). Then the extractor loaded with sample and dried is measured similarly. The ratio of sample and background spectra is calculated and converted to absorbance units to obtain a final spectrum. Finally, the peak height at 2920 cm^{-1} is then calculated with baseline correction from 2990 to 2800 cm^{-1} .



Figure 3: Sampling from bottle into syringe



Figure 4: ClearShot extractor on syringe pump



Figure 5: ClearShot extractor drying



Figure 6: Infrared measurement

Calibration and Standardization

The infrared spectra of the seven *Calibration Standard Devices (CSD)* containing a known quantity of certified oil and grease were measured and peak heights at 2920 cm^{-1} determined (Figure 7). The known concentration and measured absorbance values of each sample were plotted (Figure 8). The best fit line was used to produce the slope and intercept values for unknown sample prediction. Excellent linearity is observed between the absorbance values at 2920 cm^{-1} and the expected values of Calibration Standard Devices. Over the calibration range of 5–200 PPM an R-squared (R^2) value of 0.9997 was obtained. In practice, these slope and offset terms are uniform across spectrometers. Thus, measurement of the CSD set in a method transfer typically serves to confirm the accuracy of the method as well as its usable range.

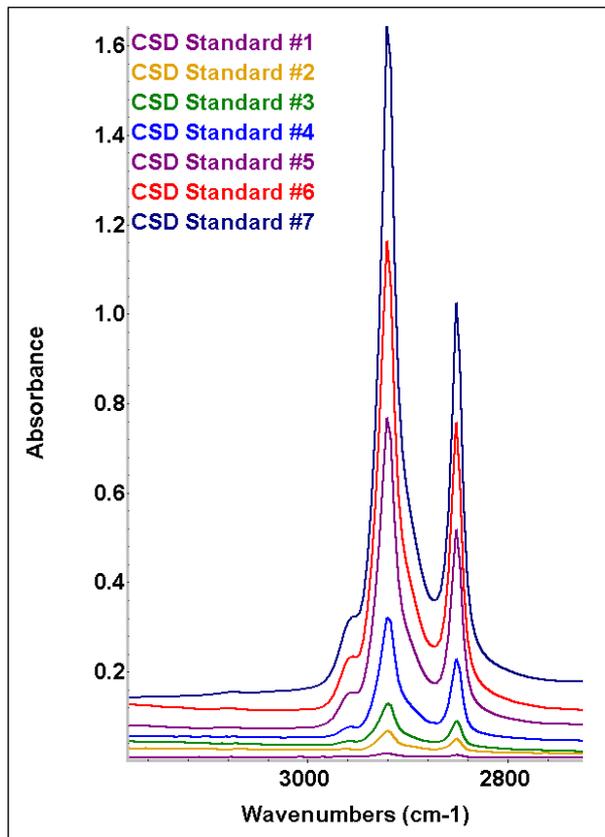


Figure 7: Overlaid spectra from Calibration Standard Devices. (Spectra offset for clarity)

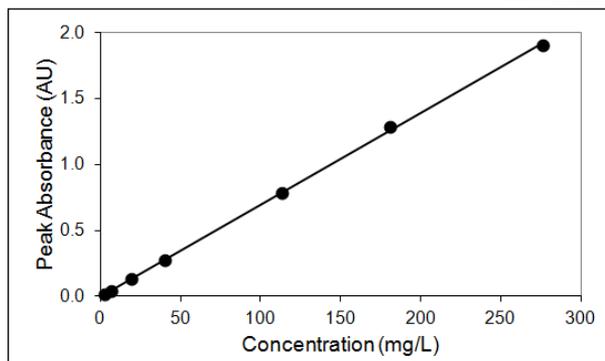


Figure 8: Plot of peak height at 2920 cm^{-1} vs. concentration for Calibration Standard Devices $R^2 = 0.9997$

Discussion

Determination of Precision and Recovery

The infrared spectra of four ClearShot extractors each processed with samples drawn from a solution of 40 mg/L oil and grease sample prepared from a 1:1 hexadecane and stearic acid spiking solution were measured. The slope and offset calibration values from the CSD set shown previously were applied to the baseline corrected peak heights at 2920 cm^{-1} . Table 1 shows the Absorbance and calculated Concentration values as well as the Average and Relative Standard Deviation for the results. The Average Percent Recovery and Relative Standard Deviation of the recoveries are shown in Table 2. These results fell well within the prescribed ASTM D7575 method limits.

Table 1

Sample	Absorbance	Concentration (mg/L)
1	0.28	40.5
2	0.26	37.6
3	0.29	41.9
4	0.28	40.5

Average Concentration = 40.1

Standard Deviation of Concentration = 1.8

Table 2

	Observed	ASTM D7575 Limits
Average Percent Recovery	100%	88–106%
Relative Standard Deviation	5%	<11%

Determination of Detection Limit (MDL) and Reporting Limit

The infrared spectra of seven ClearShot extractors processed with samples drawn from a solution of 4 mg/L oil and grease sample prepared from a 1:1 hexadecane and stearic acid solution were measured. The slope and offset calibration values from the CSD set shown previously were applied to the baseline corrected peak heights at 2920 cm^{-1} . Table 3 shows the values for calculated absorbance, concentration, Standard Deviation of Concentration, Lower Detection Limit, and Lower Reporting Limit. These results also confirm the stated Lower Reporting Limit for the ASTM D7575 method of 5.0.

Table 3

Sample	Absorbance	Concentration (mg/L)
1	0.0370	5.6
2	0.0339	5.2
3	0.0290	4.5
4	0.0373	5.7
5	0.0320	4.9
6	0.0307	4.7
7	0.0339	5.2

Standard Deviation of Concentration = 0.45

Lower Detection Limit = $3.143 \times (\text{Std. Dev}) = 1.40$

Lower Reporting Limit = $10 \times (\text{Std. Dev}) = 4.45$

Comparison to EPA 1664

In order to confirm agreement between the ASTM D7575 and EPA 1664 methods, a sample set was run by both of these methods.⁹ The results are plotted below in Figure 9 which demonstrates high correlation between these two methods ($R^2 = 0.9553$). In addition, the robustness of the ASTM D7575 method is confirmed since these samples originated from ten different source types including POTW (Public Owned Treatment Works), meat processor, petroleum plant, chemical manufacturer and others.

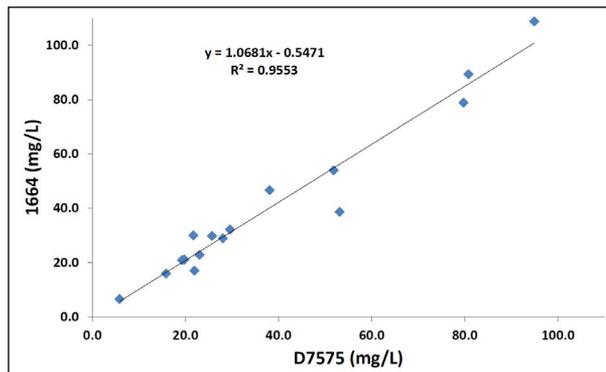


Figure 9: Comparison of predicted oil and grease values obtained from EPA 1664 vs. ASTM D7575. $R^2 = 0.9553$

Conclusions

The results of this study demonstrate that this method provides a solvent-free, accurate measurement of hydrocarbons in processed and wastewater at concentrations in the low PPM range. This analysis requires as little as five minutes per sample versus the four hours necessary with the *n*-hexane extraction gravimetric EPA method. This green method has been shown to provide equivalent accuracy to the current method EPA 1664 and has been recognized by the EPA as an alternative procedure (ATP).¹⁰

“EPA’s analysis demonstrates ASTM D7575-10 is an acceptable stand-alone method for the measurement of oil in grease in wastewater for the application reporting range (5–200 mg/L) and it produces results that are generally very close to those obtained using EPA Method 1664A for the matrices tested. Second, this method has certain advantages over the currently approved method. EPA supports pollution prevention, and is particularly persuaded by the substantial advantages associated with the green aspects of this membrane technology (e.g., it uses a solventless extraction, there is no solvent waste, and no analyst exposure to solvent). Finally, ASTM D7575-10 may offer other advantages such as ease of analysis, reduced analysis time, and lower analytical costs.”¹¹

As an added benefit, it has been shown that when considering consumables and labor expenses, the solvent-less ASTM D7575 method is less than one quarter the cost of the *n*-hexane based EPA 1664 method. The elimination of explosion-proof fume hoods and flammable storage, not included in this calculation, would be a further cost savings.

References

1. EPA Clean Water Act (CWA) <http://www.epa.gov/agriculture/lcwa.html#Summary>
2. EPA NPDES Home <http://water.epa.gov/polwaste/npdes/>
3. EPA Ozone Layer Protection Montreal Protocol <http://www.epa.gov/ozone/intpol/>
4. EPA Oil and Grease <http://water.epa.gov/scitech/methods/cwa/oil/index.cfm>
5. OSS internal document submitted to EPA estimating hexane usage based on the number of National Pollution Discharge Elimination Systems (NPDES) permits
6. ASTM Standards and Publications, ASTM D7575-11 Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination
7. Additional information at <http://www.ossmaine.com>
8. Additional information at <http://www.ossmaine.com>
9. Additional details of this study are provided in ASTM D7575
10. Federal Register / Vol. 78, No. 44 / March 6, 2013, pg. 14457–14461
11. Federal Register / Vol. 76, No. 240 / December 14, 2011, pg. 77742–77747

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Russia/CIS +43 1 333 50 34 0
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