

Infrared Spectroscopy

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Determination of Oil and Grease in Water with a Mid-Infrared Spectrometer

Introduction

The concentration of dispersed oil and grease (OG) is an important parameter for water quality and safety. OG in water can cause surface films and shoreline deposits leading to environmental degradation, and can induce human health risks when discharged in surface or ground waters.

Additionally, OG may interfere with aerobic

and anaerobic biological processes and lead to decreased wastewater treatment efficiency. Regulatory bodies worldwide set limits in order to control the amount of OG entering natural bodies of water or reservoirs through industrial discharges, and also to limit the amount present in drinking water.

OG in water is commonly determined by extraction into a non-polar, hydrocarbon-free solvent followed by measurement of the infrared absorption spectrum of the extract. The absorption between 3000 and 2900 cm^{-1} by C-H groups in the OG is correlated to the concentration of OG. There are several standard test protocols based around this methodology,¹⁻⁴ most commonly using 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) or tetrachloromethane. However, these solvents are known ozone-depleting compounds, and under the Montreal Protocol, the use of CFC-113 was phased out by 1996 and the use of tetrachloromethane will become illegal in 2010.

This application note presents the method development for the analysis of OG in water using tetrachloroethylene extraction followed by mid-infrared (mid-IR) spectrometry. Tetrachloroethylene does not have the adverse environmental effects of CFC-113 and tetrachloromethane, and is in wide use for dry-cleaning of fabrics. It is well-suited to OG determination because it is an excellent solvent for organic compounds and has no C-H groups.

Experimental

Apparatus and Reagents

The accessories and reagents used in the analysis are listed below:

- Glass separatory funnel
- Volumetric flasks 10, 25, 50 and 100 mL
- Eppendorf® micropipette
- Analytical balance
- Filter paper
- Glass funnel
- Glass wide mouth sample bottle 250 mL, with screw cap having a fluoropolymer liner
- Isooctane
- Octanoic acid
- Sodium sulfate
- Tetrachloroethylene (ACS spectroscopy grade)
- Sulfuric acid
- Water, ASTM® type II

Note: All the reagents and chemicals used were of ACS reagent grade unless otherwise stated. It is important to use a grade of tetrachloroethylene that is free from hydrocarbon contamination.

Preparation of Calibration Solutions and Spiked Aqueous Samples

A calibration stock solution of 100 mg/mL total OG was prepared by placing 0.55 mL of octanoic acid and 0.72 mL of isooctane in a 10 mL volumetric flask and filling to the mark with tetrachloroethylene. This stock solution was further diluted by pipetting 2.5 mL into a 50 mL volumetric flask and filling to the mark with tetrachloroethylene. Calibration standards were prepared from the diluted stock solution as described in Table 1 (Page 3).

A reference OG mixture was prepared by mixing equal volumes of octanoic acid and isooctane. Spiked samples were prepared by adding known volumes of this mixture to known volumes of water.

Volumetric concentrations of OG were converted to mass/volume concentrations by using values of 773 and 911 g/L for the densities of isooctane and octanoic acid, respectively.¹

Method for OG Extraction

A 250 mL sample of water or wastewater is acidified to pH 2.0 by dropwise addition of 50% sulfuric acid, and then extracted serially with three ~15 mL volumes of tetrachloroethylene. The combined extract is dried by filtering through 1 g of sodium sulfate then diluted to 50 mL in a volumetric flask. This method of extraction produces an extract solution with five times the concentration of the original oil-in-water sample.

FT-IR Measurements

Absorbance measurements were performed using the PerkinElmer® Spectrum™ 400 FT-IR/NIR spectrometer (PerkinElmer, Inc., Shelton, CT USA) in mid-IR mode.* Spectra were collected in transmission mode using a glass cell with 10 mm pathlength. Spectra were acquired over the range 3200–2700 cm⁻¹ at 8 cm⁻¹ resolution with ~1 minute acquisition time, and ratioed against a spectrum of pure solvent. The peak maximum between 2945 and 2915 cm⁻¹ was determined and used in the linear regression described on Page 3. A linear baseline fit through the points at 3100 and 2800 cm⁻¹ was subtracted before measuring the peak height.

* The Spectrum 400 is superseded by the PerkinElmer Frontier IR/NIR dual range system. The analysis is also possible using the Frontier IR system and Spectrum Two FT-IR.



Figure 1. The PerkinElmer Frontier FT-IR spectrometer.

Table 1. Calibration Standards.

Standard number	Volume of 5 mg/mL stock diluted to 10 mL	Concentration (mg/mL)	Equivalent conc. in mg/L of OG in a 250-mL water sample extracted into a 50-mL volume of solvent
Std1	0.05	0.025	5
Std2	0.10	0.050	10
Std3	0.20	0.100	20
Std4	0.30	0.150	30
Std5	0.50	0.250	50
Std6	0.60	0.300	60
Std7	0.70	0.350	70
Std8	0.80	0.400	80

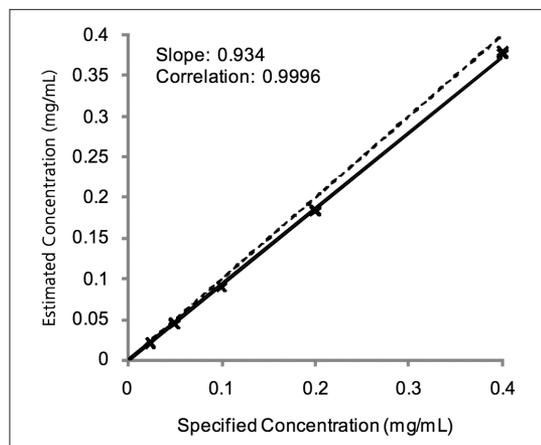


Figure 3. Plot of estimated vs. specified values for validation samples. The dashed line represents perfect agreement: the systematic deviation from this is due to the extraction efficiency being around 93%.

Results and Discussion

Calibration and Validation

Over the calibration range, excellent linearity and precision were observed (see Figures 2 and 3), with a correlation coefficient (R^2) of 0.9999 and a standard error of prediction (SEP) of 0.002 mg/mL being obtained for analysis of the extract, corresponding to 0.4 mg/L OG in water with the present extraction procedure.

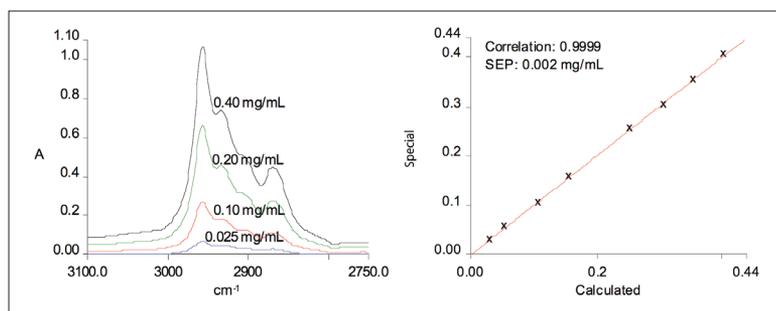


Figure 2. Spectra of calibration standards and calibration graph (calculated vs. specified concentration).

The method was validated by preparing standards of OG in water as described in the Experimental section (Page 2). Five standards over the range of 5 to 80 mg/L OG in water were prepared and processed through the entire analytical method. When the model predicted values are plotted against the true values (assuming extraction efficiency of 100%), they lie on a line with a slope of 0.93, indicating an extraction efficiency of 93%. The very high correlation coefficient indicates that the extraction efficiency is consistently near this value, and this would permit a correction of the predicted values to account for the oil not extracted. Alternatively, this factor could be built into the model by using extracted samples for calibration. After correction for the extraction efficiency, the SEP was found to be 0.004 mg/mL. In terms of the original OG in water samples, this corresponds to 0.8 mg/L.

Spike Recovery

Any analytical method involving an extraction step is at risk of negative bias introduced by incomplete extraction. In addition to the findings above, recovery studies were performed. The spiking solution was prepared by mixing equal volumes of octanoic acid and isooctane in a volumetric flask. 15 μ L (12.0 mg) of this solution was spiked into the water samples. Table 2 summarizes the results. The recoveries are high but show some variability with values ranging from 91 to 97 percent. This indicates that the solvent extraction recovers nearly all of the OG and introduces only a small negative bias to the reported result.

Table 2. Replicate Spike Recoveries.

Sample	% Recovery
Water sample 1	91.86
Water sample 2	90.82
Water sample 3	94.11
Water sample 4	93.44
Water sample 5	96.10
Water sample 6	96.06

Detection Limit

Since several sources of error in the calibration are proportional to the concentration, a calibration with a high upper limit will tend to have a higher detection limit. Thus, a series of standards at lower concentrations were prepared (Table 3) and a low-concentration model developed (Figure 4).

Table 3. Standards Used for the Detection-Limit Study.

Standard number	Concentration (mg/mL)	Equivalent conc. in mg/L of OG in a 250-mL water sample extracted into a 50-mL volume of solvent
DL1	0.002	0.4
DL2	0.003	0.6
DL3	0.004	0.8
DL4	0.005	1.0

The SEP of 0.0001 mg/mL implies a detection limit of under 0.0005 mg/mL, without considering the pre-concentration factor provided by the extraction process. Provided that the efficiency of the extraction is maintained at low concentrations, a detection limit of 0.1 mg/L for OG in water may be achievable.

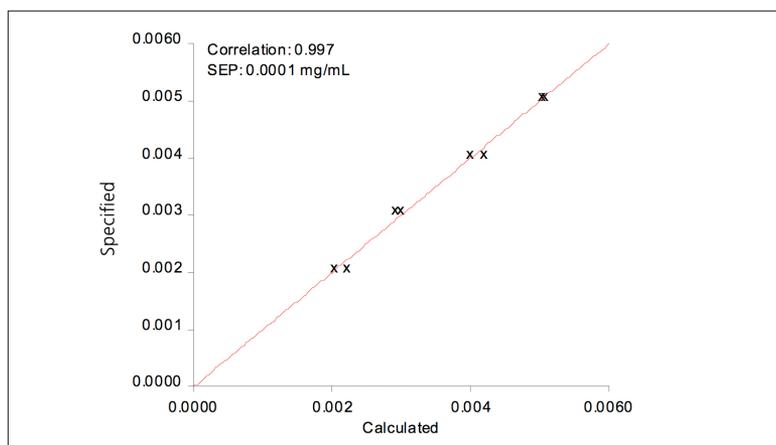


Figure 4. Estimated-vs.-specified plot for the low-concentration model (concentrations are in mg/mL oil in solvent).

Conclusion

The PerkinElmer Frontier or Spectrum Two series of FT-IR spectrometers can be utilized successfully for the determination of oil and grease in water samples. The method shows good linearity and precision, with a detection limit below 0.5 mg/L. Tetrachloroethylene was found to be a suitable solvent for this analysis, and has a much lower environmental impact than the previously favored solvents such as CFC-113 and tetrachloromethane.

References

1. ASTM® D7066-04: Standard test method for dimer/trimer of chlorotrifluoroethylene (S-316) recoverable Oil and Grease and Nonpolar material by Infrared determination, 2004.
2. APHA Method 5520C Partition-Infrared method: Standard method for the examination of Water and Wastewater, 1999.
3. EPA, Method 418.1: Petroleum Hydrocarbons (Spectrophotometric Infrared) 1978.
4. ICH Harmonised Tripartite Guideline/Validation of Analytical Procedures: Methodology Q2R.