

Application News

No. A544

Spectrophotometric Analysis

Quantitative Analysis of Oil and Grease in Water Using FTIR Based on ASTM D7575

The discharge of oil and grease into water environments such as oceans and rivers is a water quality control issue since it may lead to environmental problems including adverse effects on ecological systems and malodor. A measurement method described in JIS K 0102 "Testing Methods for Industrial Wastewater"¹ that involves determining the quantity of n-Hexane extract is one method for quantifying oil and grease in water. However, there are issues with this method including the necessity of cumbersome pretreatment and the long time required until results are obtained.

This article introduces a quantitative analysis method for oil and grease in water that employs FTIR based on the ASTM D7575 standard.² ASTM standards are set and published by ASTM International, which is the world's largest international standardization and standards-setting organization. ASTM D7575 enables quantitation of oil and grease in water with a simple measurement method that utilizes the absorption band of CH groups, thereby eliminating the need for solvent extraction.

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Overview of Testing Based on ASTM D7575

Testing was performed using the ClearShot Extraction Package³ manufactured by Orono Spectral Solutions, Inc., shown in Fig. 1. The measurement instrument, testing equipment, reagents used, and contents of the ClearShot Extraction Package are listed below.



Fig. 1 ClearShot Extraction Package

<Measurement Instrument and Testing Equipment>

- Fourier transform infrared spectrophotometer
- 1 L glass sample collection bottle
- Ultrasonic cleaner capable of heating to 40 °C and accommodating the 1 L glass sample collection bottle
- 10 mL syringe
- 10 mL and 1 mL measuring pipets
- 100 mL measuring flask

<Reagents Used>

- 12.1 M hydrochloric acid (The following items are for recovery rate verification.)
- Ion exchange water
- Acetone
- Hexadecane
- Stearic acid

<Contents of ClearShot Extraction Package>

- ClearShot™ Extraction Technology cartridges (ClearShot extractors)
- ClearShot Holding Card
- Calibration Standard Devices (CSD) Set
- Drying System

Calibration Curve Creation

After measuring the background with a new ClearShot extractor, the seven calibration standard devices (CSD) for calibration curve creation were measured using the transmittance mode. A calibration curve was created by setting a baseline between 2990 cm⁻¹ and 2800 cm⁻¹ in the obtained infrared spectra and determining the heights of the top peaks from the baseline at 2920 cm⁻¹. Table 1 lists the measurement conditions, Fig. 2 shows an enlarged view of peaks around 2920 cm⁻¹ of the standard samples, and Fig. 3 shows the calibration curve and lists the standard sample concentrations.

Table 1 Measurement Conditions

Instrument	: IRTracer-100
Resolution	: 4 cm ⁻¹
Accumulation	: (BKG) 200 times, (sample) 64 times
Apodization function	: SqrTriangle
Detector	: DLATGS

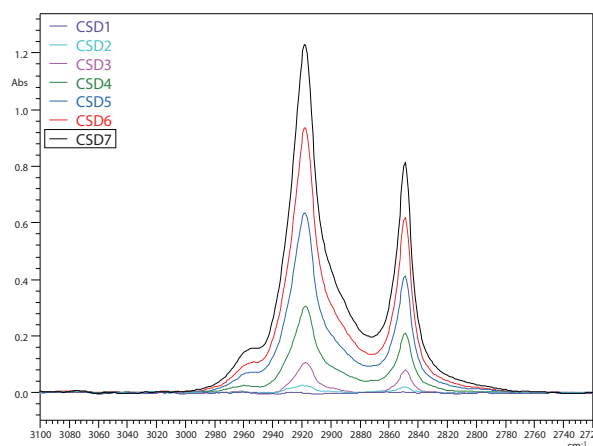
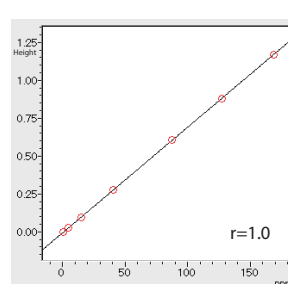


Fig. 2 Enlarged View of Peaks Around 2920 cm⁻¹



Sample	Absorbance	Concentration [ppm]
CSD1	0.0020	0.73
CSD2	0.026	4.54
CSD3	0.096	15.23
CSD4	0.28	40.56
CSD5	0.60	87.57
CSD6	0.87	127.55
CSD7	1.2	168.70

Fig. 3 Calibration Curve and Standard Sample Concentrations

■ Checking Repeatability

Repeatability of measurement was checked using standard sample CSD5. Table 2 shows the repeatability measurement results obtained by two different methods: (a) 10 consecutive measurements without removing the cartridge inserted in the sample chamber and (b) 10 measurements by removing and then reinserting the cartridge for each measurement. Fig. 4 shows the infrared spectra obtained from the 10 consecutive measurements. Variation between measurements was low and favorable repeatability was obtained even with the method in which the cartridge was removed.

Table 2 Repeatability
(a) 10 consecutive measurements without removing the sample
(b) 10 measurements with removal of the sample for each measurement

Measurement Method	Number of Measurements	Concentration [ppm]	Standard Deviation [ppm]
(a) No removal	10	95.33	0.96
(b) With removal	10	94.63	0.99

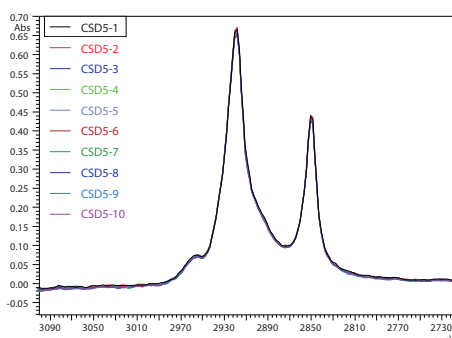


Fig. 4 Infrared Spectra of Repeated Measurements (10 Consecutive Measurements)

■ Verification of Recovery Rate

The procedure is described below.

<Sample Preparation>

- Put 400 mg \pm 4 mg of hexadecane and 400 mg \pm 4 mg of stearic acid into the 100 mL measuring flask.
- Add acetone to prepare a 1:1 solution of hexadecane and stearic acid.
- Use the ion exchange water as a solvent to adjust the solution from step ② to a concentration of 40 ppm.

<Sample Measurement>

- Put about 12 mL of sample into the 10 mL syringe and let it stand for a short while to allow any air bubbles within the sample to escape.
- Filter 10 mL of sample solution using a ClearShot extractor. Then dry the ClearShot extractor holding captured extract by blowing it with compressed air for a few minutes.
- Measure the background with a new ClearShot extractor and then measure the infrared spectrum of the dried ClearShot extractor.
- Calculate the quantitative value using the created calibration curve.

Table 3 lists the verification results of the recovery rates obtained by the above procedure. By comparing the concentrations calculated from the absorbance values and the concentrations of the samples, we obtained recovery rates between 94 % and 107 %.

Table 3 Recovery Rate Verification Results

Sample	Absorbance	Concentration [ppm]
1	0.28	41.22
2	0.25	37.65
3	0.29	42.09
4	0.29	42.88

■ Quantitative Analysis of Oil and Grease in Water

The procedure is described below.

<Sample Preparation>

- Put the measurement sample into the glass sample collection bottle and adjust to pH 2 by adding the 12.1 M hydrochloric acid.
- Put the sample collection bottle into the ultrasonic cleaner heated to 40 °C and leave it for 20 minutes.

<Sample Measurement>

- Put about 12 mL of sample into the 10 mL syringe and let it stand for a short while to allow any air bubbles within the sample to escape.
- Filter 10 mL of sample solution using a ClearShot extractor. Then dry the ClearShot extractor holding captured extract by blowing it with compressed air for a few minutes.
- Measure the background with a new ClearShot extractor and then measure the infrared spectrum of the dried ClearShot extractor.
- Calculate the quantitative value using the created calibration curve.

Quantitative analysis was performed on three samples by the above procedure. Table 4 shows the results.

Table 4 Measurement Conditions

Sample	Absorbance	Concentration [ppm]
1	0.15	22.84
2	0.49	72.70
3	0.79	115.14

■ Conclusion

The analysis method for oil and grease in water based on the ASTM D7575 standard allows simple and fast quantitation in the order of ppm without the need for solvent extraction. In this Application News, we confirmed that by using Shimadzu's FTIR and the ClearShot Extraction Package manufactured by Orono Spectral Solutions, Inc., calibration curve creation, repeatability checking, recovery rate verification, and actual quantitation of oil and grease can be done easily based on the ASTM D7575 standard.

References:

- *1 JIS K 0102 "Testing Methods for Industrial Wastewater"
- *2 ASTM D-7575 -Standard Test Method for Solvent-Free Membrane Recoverable Oil and Grease by Infrared Determination-
- *3 The ClearShot Extraction Package complies with the ASTM D7575 standard. Clearshot Extraction Technology is a registered trademark of Orono Spectral Solutions, Inc. <http://www.ossmaine.com/>

Caution 1) The ClearShot Extraction Package is not sold by Shimadzu. Please purchase it directly from Orono Spectral Solutions, Inc.

Caution 2) The cartridges included in the ClearShot Extraction Package cannot be fitted to the standard cassettes of the IRTTracer-100 and IRAffinity-1S. For details, contact your Shimadzu representative.