

OIL AND GREASE, TOTAL RECOVERABLE

Method 413.2 (Spectrophotometric, Infrared)

STORET NO. 00560

1. Scope and Application
 - 1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters, industrial and domestic wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related matter.
 - 1.2 The method is applicable to measurement of most light petroleum fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
 - 1.3 The method covers the range from 0.2 to 1000 mg/l of extractable material.
 - 1.4 While this method can be used to obtain an estimate of the oil and grease that would be measured gravimetrically, in many cases the estimate more accurately describes the parameter, as it will measure volatiles more effectively and is not susceptible to interferences such as extractable sulfur. It can be used with the Petroleum Hydrocarbon procedure to obtain an oil and grease value and a petroleum hydrocarbon value on the same sample.
2. Summary of Method
 - 2.1 The sample is acidified to a low pH (< 2) and extracted with fluorocarbon-113. The oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.
3. Definitions
 - 3.1 The definition of oil and grease is based on the procedure used. The source of the oil and/or grease, and the presence of extractable non-oily matter will influence the material measured and interpretation of results.
4. Sampling and Storage
 - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by the addition of 5 ml HCl (6.1) at the time of collection and refrigerated at 4°C.
 - 4.2 Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.
5. Apparatus
 - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
 - 5.2 Infrared spectrophotometer, scanning. Non-scanning instruments may also be used but can be subject to positive interferences in complex chemical wastewaters.
 - 5.3 Cells, 10 mm, 50 mm, and 100 mm path length, sodium chloride or infrared grade glass.
 - 5.4 Filter paper, Whatman No. 40, 11 cm.

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6. Reagents

- 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc. HCl and distilled water.
- 6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b. p. 48°C.
- 6.3 Sodium sulfate, anhydrous crystal.
- 6.4 Calibration mixtures:
 - 6.4.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.
 - 6.4.2 Stock standard: Pipet 1.0 ml reference oil (6.4.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
 - 6.4.3 Working standards: Pipet appropriate volumes of stock standard (6.4.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure

- 7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.
- 7.2 Pour the sample into a separatory funnel.
- 7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.
- 7.4 Filter the solvent layer into a 100 ml volumetric flask through a funnel containing solvent-moistened filter paper.
NOTE: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.
- 7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent in the volumetric flask.
- 7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml fluorocarbon-113 and collect the rinsings in the flask. Dilute the extract to 100 ml, and stopper the flask.
- 7.7 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

<u>Pathlength</u>	<u>Range</u>
10 mm	2–40 mg
50 mm	0.4–8 mg
100 mm	0.1–4 mg

- 7.8 Scan standards and samples from 3200 cm^{-1} to 2700 cm^{-1} with fluorocarbon-113 in the reference beam and record the results on absorbance paper. The absorbances of samples

and standards are measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum at 2930 cm^{-1} and subtracting the baseline absorbance at that point. For an example of a typical oil spectrum and baseline construction, see Gruenfeld⁽⁹⁾. Non-scanning instruments should be operated according to manufacturer's instructions, although calibration must be performed using the standards described above (6.4). If the absorbance exceeds 0.8 for a sample, select a shorter pathlength or dilute as required.

7.9 Use a calibration plot of absorbance vs. mg oil prepared from the standards to determine the mg oil in the sample solution.

8. Calculation

$$8.1 \text{ mg/l total oil and grease} = \frac{R \times D}{V}$$

where:

R = oil in solution, determined from calibration plot, in milligrams.

D = extract dilution factor, if used.

V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary, in liters.

9. Precision and Accuracy

9.1 The two oil and grease methods in this manual were tested by a single laboratory (EMSL) on sewage. This method determined the oil and grease level in the sewage to be 17.5 mg/l. When 1 liter portions of the sewage were dosed with 14.0 mg of a mixture of #2 fuel oil and Wesson oil, the recovery was 99% with a standard deviation of ± 1.4 mg/l.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 516, Method 502B, (1975).
2. American Petroleum Institute, "Manual on Disposal of Refinery Wastes", Vol. IV, Method 733-58 (1958).
3. Gruenfeld, M., "Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectroscopy", Environ. Sci. Technol. 7, 636 (1973).