

PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE

Method 418.1 (Spectrophotometric, Infrared)

STORET NO. 45501

1. Scope and Application
 - 1.1 This method is for the measurement of fluorocarbon-113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.
 - 1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
 - 1.3 The method is sensitive to levels of 1 mg/l and less, and may be extended to ambient monitoring.
2. Summary of Method
 - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbant. Infrared analysis of the extract is performed by direct comparison with standards.
3. Definitions
 - 3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.
 - 3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.
4. Sampling and Storage
 - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample.
 - 4.2 A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of 5 ml HCl (6.1). A delay of greater than 48 hours also requires refrigeration for sample preservation.
5. Apparatus
 - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
 - 5.2 Filter paper, Whatman No. 40, 11 cm.
 - 5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2950 cm^{-1} .
 - 5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
 - 5.5 Magnetic stirrer, with Teflon coated stirring bars.
6. Reagents
 - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

Issued 1978

- 6.2 Fluorocarbon-113, (1,1,2-trichloro-1,2,2-trifluoroethane), b.p. 48°C.
- 6.3 Sodium sulfate, anhydrous crystal.
- 6.4 Silica gel, 60–200 mesh, Davidson Grade 950 or equivalent. Should contain 1–2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.
- 6.5 Calibration mixtures:
 - 6.5.1 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.
 - 6.5.2 Stock standard: Pipet 1.0 ml reference oil (6.5.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.
 - 6.5.3 Working standards: Pipet appropriate volumes of stock standard (6.5.2) 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 through a funnel containing solvent-moistened filter paper into a 100 ml volumetric flask.

NOTE 1: 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 into the volumetric flask.
- 7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml solvent and collect the rinsings in the flask. Dilute the extract to 100 ml. If the extract is known to contain greater than 100 mg of non-hydrocarbon organic material, pipet an appropriate portion of the sample to a 100 ml volumetric and dilute to volume.
- 7.7 Discard about 5–10 ml solution from the volumetric flask. Add 3 g silica gel (6.4) and a stirring bar; stopper the volumetric flask, and stir the solution for a minimum of 5 min on a magnetic stirrer.

- 7.8 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	0.5-8 mg
100 mm	0.1-4 mg

Calibrate the instrument for the appropriate cells using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm^{-1} . Prepare a calibration plot of absorbance vs. mg petroleum hydrocarbons per 100 ml solution.

- 7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds 0.8 prepare an appropriate dilution.

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

- 7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8. Calculations

- 8.1 Calculate the petroleum hydrocarbons in the sample using the formula:

$$\text{mg/l Petroleum Hydrocarbons} = \frac{R \times D}{V}$$

where:

R = mg of Petroleum Hydrocarbons as determined from the calibration plot (7.10).

D = extract dilution factor, if used.

V = volume of sample, in liters.

9. Precision and Accuracy

- 9.1 Precision and accuracy data are not available at this time.