

METHOD 8440

TOTAL RECOVERABLE PETROLEUM HYDROCARBONS BY INFRARED SPECTROPHOTOMETRY

1.0 SCOPE AND APPLICATION

1.1 Method 8440 (formerly Draft Method 9073) is used for the measurement of total recoverable petroleum hydrocarbons (TRPHs) extracted with supercritical carbon dioxide from sediment, soil and sludge samples using Method 3560.

1.2 Method 8440 is not applicable to the measurement of gasoline and other volatile petroleum fractions, because of evaporative losses.

1.3 Method 8440 can detect TRPHs at concentrations of 10 mg/L in extracts. This translates to 10 mg/Kg in soils when a 3 g sample is extracted by SFE (assuming 100 percent extraction efficiency), and the final extract volume is 3 mL.

1.4 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Soil samples are extracted with supercritical carbon dioxide using Method 3560. Interferences are removed with silica gel, either by shaking the extract with loose silica gel, or by passing it through a silica gel solid-phase extraction cartridge. After infrared (IR) analysis of the extract, TRPHs are quantitated by direct comparison with standards.

3.0 INTERFERENCES

3.1 The analyte class being measured (TRPHs) is defined within the context of this method. The measurement may be subject to interferences, and the results should be interpreted accordingly.

3.2 Determination of TRPHs is a measure of mineral oils only, and does not include the biodegradable animal greases and vegetable oils captured in oil and grease measurements. These non-mineral-oil contaminants may cause positive interferences with IR analysis, if they are not completely removed by the silica gel cleanup.

3.3 Method 8440 is not appropriate for use in the analysis of gasoline and other volatile petroleum fractions because these fractions evaporate during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Infrared spectrophotometer - Scanning or fixed wavelength, for measurement around 2950 cm^{-1} .

4.2 IR cells - 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or IR-grade glass.

4.3 Magnetic stirrer with polytetrafluoroethylene (PTFE)-coated stirring bars.

4.4 Optional - A vacuum manifold consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge is recommended for use when silica gel cartridges are used. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.0 REAGENTS

5.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Tetrachloroethylene, C_2Cl_4 - spectrophotometric grade, or equivalent.

5.3 Raw materials for reference oil mixture - spectrophotometric grade, or equivalent.

5.3.1 n-Hexadecane, $CH_3(CH_2)_{14}CH_3$

5.3.2 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$

5.3.3 Chlorobenzene, C_6H_5Cl

5.4 Silica gel.

5.4.1 Silica gel solid-phase extraction cartridges (40 μm particles, 60 A pores), 0.5 g, Supelco, J.T. Baker, or equivalent.

5.4.2 Silica gel, 60 to 200 mesh, Davidson Grade 950 or equivalent (deactivated with 1 to 2 percent water).

5.5 Calibration mixtures:

5.5.1 The material of interest, if available, or the same type of petroleum fraction, if it is known and original sample is unavailable, shall be used for preparation of calibration standards. Reference oil is to be used only for unknowns. Whenever possible, a GC fingerprint should be run on unknowns to determine the petroleum fraction type.

5.5.2 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. Refrigerate at 4°C when not in use.

5.5.3 Stock standard - Pipet 0.5 mL calibration standard (Section 5.5.1 or 5.5.2) into a tared 100 mL volumetric flask and stopper immediately. Weigh and dilute to volume with tetrachloroethylene.

5.5.4 Working standards - Pipet appropriate volumes of stock standard (Sec. 5.5.3) into 100 mL volumetric flasks according to the cell size to be used. Dilute to volume with

tetrachloroethylene. Calculate the concentrations of the standards from the stock standard concentrations.

5.6 Calibration of silica gel cleanup

5.6.1 Prepare a stock solution of corn oil and mineral oil by placing about 1 mL each (0.5 to 1 g) of corn oil and mineral oil into a tared 100 mL volumetric flask. Stopper the flask and weigh to the nearest milligram. Dilute to the mark with tetrachloroethylene, and shake the contents to effect dissolution.

5.6.2 Prepare additional dilutions to cover the range of interest.

5.6.3 Transfer 2 mL (or other appropriate volume) of the diluted corn oil/mineral oil samples to vials.

5.6.4 Add 0.3 g of loose silica gel to the vials of diluted corn oil/mineral oil samples and shake the mixture for 5 minutes, or pass the extract through a 0.5 g silica gel solid-phase extraction cartridge (conditioned with 5 mL of tetrachloroethylene). Elute with tetrachloroethylene. Collect three 3 mL (or other appropriate volume) fractions of eluant. When using loose silica gel, filter the extract through a plug of precleaned silanized glass wool in a disposable glass pipette.

5.6.5 Fill a clean IR cell with the solution. Determine the fraction(s) in which the hydrocarbons will elute without corn oil being present using the absorbances of each fraction of the extract at $2800\text{-}3000\text{ cm}^{-1}$ (hydrocarbon range) and $1600\text{-}1800\text{ cm}^{-1}$ (ester range). If the absorbance indicates that the absorptive capacity of the silica gel has been exceeded or that the silica gel is not absorbing the corn oil (corn oil is present in the extract), select new silica gel or solid phase cartridges.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Solid samples should be collected and stored as any other solid sample containing semivolatiles. See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

6.2 Samples should be analyzed with minimum delay, upon receipt in the laboratory, and must be kept refrigerated prior to analysis.

7.0 PROCEDURE

7.1 Prepare samples according to Method 3560.

7.2 Add 0.3 g of loose silica gel to the extract and shake the mixture for 5 minutes, or pass the extract through a 0.5 g silica gel solid-phase extraction cartridge (conditioned with 5 mL of tetrachloroethylene). When using loose silica gel, filter the extract through a plug of precleaned silanized glass wool in a disposable glass pipette.

7.3 After the silica gel cleanup, fill a clean IR cell with the solution and determine the absorbance of the extract. If the absorbance exceeds the linear range of the IR spectrophotometer, prepare an appropriate dilution and reanalyze. The possibility that the absorptive capacity of the

silica gel has been exceeded can be tested at this point by repeating the cleanup and determinative steps.

7.4 Select appropriate working standard concentrations and cell pathlengths according to the following ranges:

<u>Pathlength (mm)</u>	<u>Concentration range ($\mu\text{g/mL}$ of extract)</u>	<u>Volume (mL)</u>
10	5 to 500	3
50	1 to 100	15
100	0.5 to 50	30

Calibrate the instrument for the appropriate cells using a series of working standards. Determine absorbance directly for each solution at the absorbance maximum at about 2950 cm^{-1} . Prepare a calibration plot of absorbance versus concentration of petroleum hydrocarbons in the working standards.

7.5 Determine the concentration of TRPHs in the extract by comparing the response against the calibration plot.

7.6 Calculate the concentration of TRPHs in the sample using the formula:

$$\text{Concentration (mg/Kg)} = \frac{R \times D \times V}{W}$$

where:

R = mg/mL of TRPHs as determined from the calibration plot

V = volume of extract, in milliliters

D = extract dilution factor, if used

W = weight of solid sample, in kilograms.

7.7 Recover the tetrachloroethylene used in this method by distillation or other appropriate technique.

8.0 QUALITY CONTROL

8.1 Reagent blanks or matrix-spiked samples must be subjected to the same analytical procedures as those used with actual samples.

8.2 Refer to Chapter One for specific Quality Control procedures and to Method 3500 for sample preparation procedures.

8.3 Based on manufacturer's recommendation, each laboratory should establish quality control practices necessary to evaluate the scanning or fixed wavelength infrared spectrophotometer.

9.0 METHOD PERFORMANCE

9.1 Table 1 presents a comparison of certified values and the values obtained using Methods 3560 and 8440. Data are presented for both Freon-113 and tetrachloroethylene, since both solvents were found to be an acceptable collection solvent. However, only tetrachloroethylene is recommended as a collection solvent for TRPHs in Method 3560.

9.2 Table 2 presents precision and accuracy data from the single-laboratory evaluation of Methods 3560 and 8440 for the determination of petroleum hydrocarbons from spiked soil samples. These data were obtained by extracting samples at 340 atm/80°C/60 minutes (dynamic).

10.0 REFERENCES

1. Rohrbough, W. G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society, Washington, DC, 1986.
2. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development, Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information, Cincinnati, OH, 1983; EPA-600/4-79-020.

TABLE 1
 CERTIFIED AND SPIKE VALUES COMPARED TO RESULTS
 OBTAINED BY METHODS 3560/8440

Reference Material	Spike conc. or certified conc. (mg/kg)	Methods 3560/8440 (mg/kg)
Environmental Resource Assoc. TPH-1 (lot 91012)	1,830	1,920 ±126 ^a
Environmental Resource Assoc. TPH-2 (lot 91012)	2,230	2,150 ±380 ^a
Clay spiked with kerosene ^b	100	86.0; 93.0
Clay spiked with light gas oil ^c	100	84.0; 98.0
Clay spiked with heavy gas oil ^d	100	103; 108
Environmental Resource Assoc. TPH-1 (lot 91017) ^e	614	562; 447
Environmental Resource Assoc. TPH-2 (lot 91017) ^e	2,050	1,780; 1,780

^a Three 60 minute extractions. The extracted material was collected in Freon-113; the concentrations were determined against the reference oil standard.

^b Duplicate 30 minute extractions. The extracted material was collected in tetrachloroethylene; the concentrations were determined against standard made from the spiking material.

^c Six 30 minute extractions. The extracted material was collected in tetrachloroethylene; the concentrations were determined against a standard made from the spiking material.

^d Four 30 minute extractions. The extracted material was collected in tetrachloroethylene; the concentrations were determined against a standard made from the spiking material.

^e Three 30 minute extractions. The extracted material was collected in tetrachloroethylene; the concentrations were determined against the reference oil standard.

TABLE 2

SINGLE-LABORATORY METHOD ACCURACY AND PRECISION FOR
METHODS 3560/8440 FOR SELECTED MATRICES

Matrix	Spike conc. or certified conc. (mg/kg)	Spike Material	Method accuracy (% recovery)	Method precision (% RSD)
Clay soil ^a	2,500	Motor oil	104	8.5
ERA TPH-1 ^a (lot 91016)	2,350	Vacuum oil	80.3	19.7
ERA TPH-2 ^a (lot 91016)	1,450	Vacuum oil	88.6	19.6
SRS103-100 ^b	32,600	c	94.2	4.0

^a Eight determinations were made using two different supercritical fluid extraction systems. The extracted material was collected in Freon-113.

^b Ten determinations were made using three different supercritical fluid extraction systems. The extracted material was collected in Freon-113.

^c This is a standard reference soil certified for polynuclear aromatic hydrocarbons. No spike was added.

METHOD 8440

TOTAL RECOVERABLE PETROLEUM HYDROCARBONS
BY INFRARED SPECTROPHOTOMETRY

