UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION I
J.F. KENNEDY FEDERAL BUILDING, BOSTON, MASSACHUSETTS 02203-2211

March 4, 1991

Christopher Marraro, Esq.
Kaye, Scholer, Fierman, Hays & Handler
901 Fifteenth St., NW, Suite 1100
Washington, DC 20005

Re: Pine Street Barge Canal Superfund Site

Dear Mr. Marraro:

This is is response to your letter of November 16, 1990, concerning certain analytical methods used by EPA's contractors in performing the RI/FS for the Pine Street Superfund Site.

EPA disagrees that the analytical method you refer to was inadequately described in the RI/FS Work Plan and QAPP prepared by Metcalf & Eddy. EPA believes that the procedures used by by its contractors were adequately described in those documents, especially Appendix G. However, in order to address your concern, EPA has asked Metcalf & Eddy provide further information on these processes. Enclosed please find a copy of two letters and some documentation from M&E which explains the procedure used to try to distinguish between fuel oil and coal tar wastes.

Second, EPA disagrees with your contention that Section 105(a) of CERCLA requires that any analytical method to be used in the course of an RI/FS must be specified in the National Contingency Plan ("NCP"). As you know, each Superfund site presents a myriad of complex technical issues. This is recognized in the language of the NCP which makes clear that EPA may conduct field investigations, as appropriate, to characterize the nature of and threat posed by the hazardous substances and hazardous materials at the Site. 40 C.F.R. § 300.430(d).

Finally, as I indicated to you on the telephone when we spoke in November, EPA is using the extent of coal tar contamination as a working hypothesis in defining the Site. However, the final definition of the Site will not be known until the completion of the RI/FS at the earliest, since its exact boundaries cannot be not known until investigatory studies are completed.

Sincerely,

Margery L. Adams
Assistant Regional Counsel

cc: Ross Gilleland, Remedial Project Manager

004609-0010-003-003

January 18, 1991

Mr. Ross Gilleland
Remedial Project Manager
USEPA Region I (HPC)
JFK Federal Building
Boston, Massachusetts 02203-2211

Subject: Contract No. 68-W9-0036
Work Assignment No. 10-1L19
Pine Street Supplemental RI/FS

Dear Ross:

This letter responds to points raised by the attorney for Ultramar Petroleum, Inc. in a letter to EPA dated November 16, 1990. You requested that M&E provide a technical response to specific comments on Page 2 of the letter. These comments alleged inadequate documentation of the method developed by Enseco and used by Metcalf & Eddy to distinguish between fuel oil and coal tar in soil samples.

Metcalf & Eddy provided Killum Associates (consultants to Ultramar) with the Final QAPP. An updated Appendix G describing the analytical method for discerning fuel oil from coal tar was provided on 10/30/90 with final corrections sent 11/7/90. The method is not "standard"; however, it is a modification of the standard method ASTM 3328. Modifications that were made to the ASTM method changed the procedures only slightly and should not have hindered the ability of a laboratory to perform the analysis. The only changes that were made to the ASTM Method 3328 were the following:

- GC temperature ramping rate is slightly different.
- The DB5 capillary column is used to increase resolution capabilities rather than the OV-101, as outlined in the original method.
- The ASTM method is written to measure water born oils and not oils in soils. Enseco included a standard soxlet extraction step to quantitively remove the oil from the soil matrix prior to analysis.

It should also be noted that Enseco elaborated on the ASTM method such that it provided a more detailed description of the procedures than was outlined in the original ASTM method.

Metcalf & Eddy does not feel that the modified method provided to Ultramar via Killum was inadequately described; a qualified and properly equipped laboratory would be able to perform the fuel oil versus coal tar analysis.

I hope this response is sufficient for your needs. If you need further information, please call Andrew Beliveau, the ARCS Lead Chemist, or me for further information.

Very truly yours,

METCALF & EDDY, INC.

Patrick O. Gwinn
Site Chemist

Martha L. Zirbel, P.E.
Project Manager

MLZ:POG:jjf

cc: A. Beliveau
C. Hagger
Contract M&E Correspondence
WA#10-1L19

FEB 2 6 REC'D

Metcalf & Eddy

004609-0010-003-004

February 22, 1991

Mr. Ross Gilleland
Remedial Project Manager
USEPA Region I (HPS-CAN1)
JFK Federal Building
Boston, Massachusetts 02203-2211

Subject: Contract No. 68-W9-0036
Work Assignment No. 10-1L19
Pine Street Supplemental RI/FS

Dear Ross:

This letter is in response to your need for further clarification on differences between the ENSECO method for fuel oil versus coal tar and the ASTM Method D-3328. Included is a more detailed description of each of the major deviations of the two methods. Also included are copies of both the ASTM method and a copy of the ENSECO procedure.

Deviations from the ASTM Method D-3328 are as follows:

- The GC temperature programming is slightly different. The ASTM method calls for an initial column temperature of 75°C which is held for the first two minutes of the sample run. As the run continues, the GC is programmed such that the column temperature increases until a final temperature of 250°C is obtained. The ASTM method does not include a ramping rate. The ENSECO method calls for an initial column temperature of 300°C. The final temperature is held for ten minutes. This provides better separation of the lighter components and minimizes the total analysis time for the fraction.

- The ASTM method calls for the use of OV-101 capillary column (0.5 mm x 16 m). ENSECO uses a 0.32 mm x 30 m DB-5 capillary column to increase overall column efficiency and resolution.

- ENSECO adds a soil extraction procedures as the ASTM method is written for aqueous samples only.

Generally, the ENSECO procedure is written to provide the user with more specific information concerning the extraction and analysis. The ASTM method for using a capillary column is explained in Method B of the ASTM procedure. It is clear from comparing the two enclosed procedures that the ENSECO method is written with greater detail which we believe should enable a capable laboratory to perform the analysis.

[illegible] Square Wakefield, MA 01880
Mailing Address: PO Box 4043, Medford, MA 01888-4043
[illegible] FAX (617) 245-6293

I hope this information is sufficient for your needs. If you need further information, please call Andrew Beliveau, the ARCS Lead Chemist, or me for further information.

Very truly yours,

METCALF & EDDY, INC.

Patrick O. Gwinn
Site Chemist

Martha L. Zirbel, P.E.
Project Manager

POG:jjf

cc: A. Beliveau
C. Hagger
Contract M&E Correspondence
WA#10-1L19 File

Designation: D 3415 – 79

Standard Practice for IDENTIFICATION OF WATERBORNE OILS[1]

This standard is issued under the fixed designation D 3415; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the broad concepts of sampling and analyzing waterborne oils for identification and comparision with source oils. Detailed procedures are not discussed in this practice. A general approach is given to aid the investigator in planning a program to solve the problem of chemical characterization and to determine the source of a waterborne oil sample.

1.2 This practice is applicable to all waterborne oils taken from water bodies, either natural or man-made, such as open oceans, estuaries or bays, lakes, rivers, smaller streams, canals; or from beaches, marshes, or banks lining or edging these water systems. Generally, these waterborne oils float on the surface of the waters or collect on the land surfaces adjoining the waters, but occasionally these oils, or portions, are emulsified or dissolved in the waters, or are incorporated into the sediments underlying the waters, or into the organisms living in the water or sediments.

1.3 This practice as presently written proposes the use of specific analytical techniques described in the accompanying methods. As new techniques for characterizing waterborne oils are developed and written up as test methods, revision of this practice will likely be needed.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1129 Definitions of Terms Relating to Water[2]

D 3325 Practice for Preservation of Waterborne Oil Samples[3]

D 3326 Practices for Preparation of Sample for Identification of Waterborne Oils[3]

D 3327 Method for Analysis of Selected Elements in Waterborne Oils[3]

D 3328 Method for Comparison of Waterborne Petroleum Oils by Gas Chromatography[3]

D 3414 Method for Comparison of Waterborne Oils by Infrared Spectroscopy[3]

E 380 Metric Practice[4]

3. Definitions

3.1 *Waterborne oil*—any oil, whether or not derived from petroleum, carried by a water system (for example: ocean, bay, lake, river, etc.) usually at the surface but occasionally emulsified or dissolved in the water. The waterborne oil can also be found on beaches or banks edging the water body, in the sediments underlying the water, or in the organisms living in the water or in the sediments.

3.2 For definitions of other terms used in this practice, refer to Definitions D 1129, and to Methods D 3325, D 3326, D 3327 and D 3328. For an explanation of the metric system including units, symbols, and conversion factors, see Standard E 380.

4. Plan for Identification of Waterborne Oils

4.1 The plan for identifying waterborne oils is outlined in Fig. 1.

4.2 *Sampling*—Collect a representative sample of oil from the surface of the water, from the beach, or from the bottom sediments. Because of the wide variety of oils carried and used by shipping and because of the possibility of pollution also arising from industrial activity, samples of suspect source

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water, and is the direct responsibility of Subcommittee D 19.05 on Identification of Waterborne Oils.

Current edition approved Nov. 30, 1979. Published March 1980. Originally published as D 3415 – 75 T. Last previous edition D 3415 – 75 T.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 14.02 (Changes in Vol 11.01).

ple *must* be collected so that comparisons can be made between the waterborne oil in question and the suspect source oils.

4.3 *Preservation of Sample*—Protect the waterborne oil, as well as the suspect source oils, against possible contamination or microbial degradation, or both, by proper preservation methods as described in Method D 3325.

4.4 *Preparation of Sample*—Prepare the waterborne oil, as well as any suspect source oils, for analyses by methods described in Method D 3326. If possible, retain a neat portion of the oil for analyses. Dissolve the remainder of the oil in chloroform and centrifuge or reflux with an aromatic distillate to remove free water, solids, and debris. Distill the sample solution to remove solvent. This treatment is needed to bring the waterborne oil sample and any suspect samples to comparable conditions for subsequent comparison. If the quantity of suspect oil is less than 50 mL, the distillation step will likely need to be omitted.

4.5 *Analysis of Sample:*

4.5.1 If a neat sample of the waterborne oil can be obtained without treatment to remove water, solids, and debris, analyze it, as well as any suspect source oils, by gas chromatography, Method A, of Method D 3328, and by infrared analysis, Method D 3414. Interpretation of the gas chromatograms and infrared spectra of the waterborne oil and the suspect source oils should provide information as to whether the waterborne oil is from a petroleum source, whether its carbon-number range is similar to distillate, residual, or crude oil, and whether it resembles any of the possible suspect source oils. If the waterborne oil is weathered, it may not be possible to determine if it is a crude oil or a residual oil by gas chromatography. Odor and physical appearance may help to determine if the waterborne oil is actually from a petroleum source.

4.5.2 If a neat sample of the waterborne oil cannot be obtained, analyze the sample, after centrifuging or refluxing and removing the solvent by distillation, by the same gas chromatographic and infrared methods.

4.6 For final identification with possible source, the distilled samples may be analyzed (*1*) by gas chromatography, Methods D 3328, Method A or B, or both; (*2*) for contents of nitrogen, sulfur, vanadium, and nickel, Methods D 3337; (*3*) by infrared spectroscopy, Methods D 3414 and (*4*) by other assorted analytical techniques, including fluorescence spectrometry of aromatic hydrocarbons and flame photometric determination of sulfur compounds, methods that are being used in different laboratories, but as yet have not been written up as ASTM methods of analysis.

5. Significance

5.1 Identification of a recovered oil is determined by comparison with known oils selected because of their possible relationship to the particular recovered oil, for example, suspected or questioned sources. Thus, samples of such known oils *must* be collected and submitted along with the unknown for analysis. It is unlikely that identification of the source of an unknown oil by itself can be made without matching, that is, solely with a library of analyses.

5.2 Many similarities (within uncertainties of sampling and analysis) will be needed to establish identity beyond reasonable doubt. The analyses described will distinguish many, but not all samples. For cases in which these methods do not clearly identify a pair of samples, and for important cases where additional comparisons are needed to strengthen conclusions, other analyses will be required. Additional methods in the literature, but not included in ASTM standards, are listed in the References (1) through (10).

REFERENCES

It may be desired to consider other methods of analysis beyond those in the *Annual Book of ASTM Standards*, Part 31. A wide variety of techniques is included in the following list:

(1) Adlard, E. R., "A Review of the Methods for the Identification of Persistent Hydrocarbon Pollutants on Seas and Beaches," *Journal of the Institute of Petroleum*, JIPEA, Vol 58, 1972, p. 63.

(2) Adlard, E. R., Crosser, L. P., and Matthews, P. H. D., "Identification of Hydrocarbon Pollutants on Seas and Beaches by Gas Chromatography," *Analytical Chemistry*, ANCHA, Vol 44, 1972, p. 64.

(3) Bentz, A. P., "Oil Spill Identification," *Analytical Chemistry*, ANCHA, Vol 48, 1976, pp. 454A–472A.

(4) Coakley, W. A., "Comparative Identification of Oil Spills by Fluorescence Spectroscopy Fingerprinting," *Proceedings of Joint Conference on Prevention and Control of Oil Spills*, Am. Petroleum Inst. 1973, p. 215.

(5) Dean, J. N. and Reid, W. K., "A Rapid Method of Identification of Total Crude Oils and Crude Oil Fractions by Gel-Permeation Chromatography," *Separation Science*, SPYOA, Vol 5, 1970, p. 825.

(6) Gruenfeld, M., "Identification of Oil Pollutants: A review of Some Recent Methods," *Proceedings of Joint Conference on Prevention and Control of Oil Spills*, Am Petroleum Inst. 1973, p. 179.

(7) Kahn, L., McKenna, G. F., and Casper, L., "Characterization and Identification of Oils Obtained from the Environment," American Chemical Society Meeting in Houston, Tex., Feb. 22, 1970.

(8) Kawahara, F. K., "Characterization and Identification of Certain Petroleum Products by Means of Gas Chromatographic Analyses of Minor Components," preprint, *American Chemical Society, Division of Water, Air and Waste Chemistry ACWCA*, Los Angeles, Calif. 1971.

(9) Levy, E. M., "Identification of Petroleum Products in Marine Environment by Absorption Spectrophotometry," *Water Research*, WATRA, Vol 6, 1972, p. 57.

(10) Zitko, V., and Carson, W. V., "The Characterization of Petroleum Oils and Their Determination in the Aquatic Environment," *Tech. Report No. 217* Fisheries Research Board of Canada, 1970.

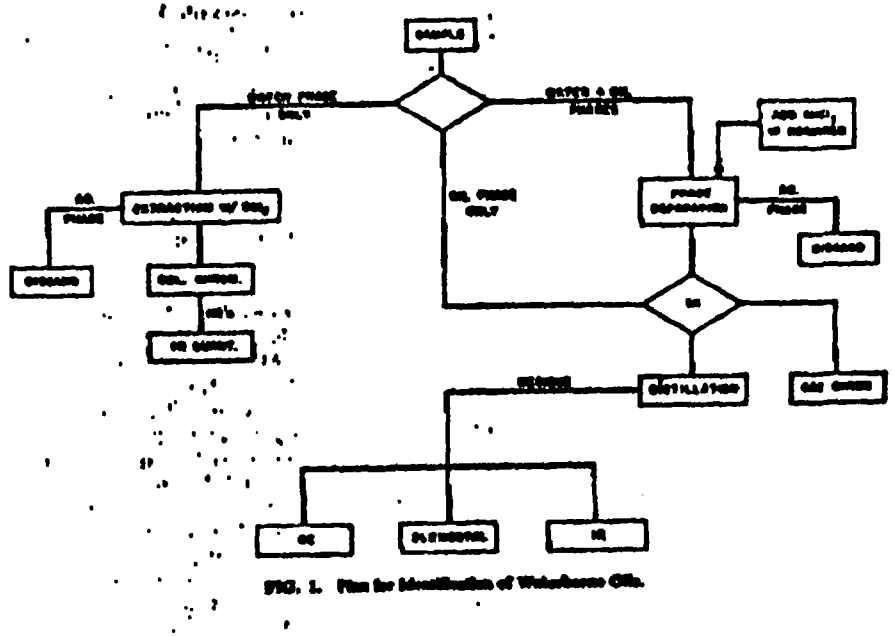

FIG. 1. Plan for Identification of Waterborne Oils.

13.10.4 Place the samples over a low flame (Note 13). Heat carefully to avoid loss of sample due to spattering. When the samples begin to boil, ignite them and allow them to burn gently until dry. Heat the residue gently with a burner until SO_2 fumes are no longer evolved.

13.10.5 Place the dishes in a muffle furnace at 540°C overnight to burn off the remaining carbon. Cool the dishes in a draft-free place. Carefully gather the ash from each dish and place it in small, labelled bottles.

13.10.6 Prepare the spectrometer as in 13.6.2.

13.10.7 Set the counter tube electronics for Ca, Ni, and V.

13.10.8 Fasten a 1¼-in. (9.7-cm²) square of polyester film on a liquid cell with a retaining ring. Secure excess film to the cell with transparent adhesive tape. Remove the ring and spread the ash on the film. Cover with another film held down by a retaining ring. The sample should thus be suspended evenly between two variable-free films with a minimum of air between films.

13.10.9 Insert the cell into the spectrometer and allow the appropriate time (approximately 1 min) for the helium to flush all air from the sample chamber.

13.10.10 Record the intensities at the five goniometer settings of 48.67, 52.79, 55.00, 74.94 and 76.94° for 100 s each (see Note 13).

13.11 *Calculations* (Concentrations < 5 ppm):

13.11.1 Subtract the background reading (in hertz) at 55.00° from the gross intensities of nickel and cobalt. This gives the net intensity for each element in hertz. Subtract the background reading at 74.94° from the vanadium gross intensity to obtain the vanadium net intensity.

13.11.2 Determine intensity ratio by dividing the net intensities for nickel and vanadium by the net intensity for cobalt.

13.11.3 Enter the calibration curves with the ratios determined above and read the concentration of each element in the sample.

13.11.4 If the sample weight was not 20 ± 0.2 g, multiply the values read from the curves by 20/sample weight, g.

13.12 *Precision* (Concentration < 5 ppm)—The repeatability has not been established, but duplicate results by the same operator should not be considered suspect unless they differ by more than the following amounts:

Amount of Element	Repeatability
< 0.15 ppm Ni or V	0.02 ppm
> 0.15 ppm Ni or V	15 % of the mean value

TABLE 1 Nickel Metallo-Organic

Standard	ppm	Nickel (6 %), g
1	100	0.6667
2	200	1.3333
3	300	2.0000

TABLE 2 Vanadium Alkylallo-Organic

Standard	ppm	Vanadium (7 %), g
1	100	1.3333
2	200	2.6667
3	300	4.0000

TABLE 3 Composition of Calibration Standard Solution

Element	Compound	Weight, g	ppm equivalent in 20-g sample		
			1.0 mL	0.6 mL	0.2 mL
Nickel	nickel nitrate·6H₂O	0.0996	0.5	0.3	0.1
Vanadium	ammonium vanadate	0.0228	0.5	0.3	0.1

Designation: D 3328 – 78 (Reapproved 1982)[ε]

Standard Methods for COMPARISON OF WATERBORNE PETROLEUM OILS BY GAS CHROMATOGRAPHY[1]

This standard is issued under the fixed designation D 3328; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[ε] NOTE—Editorial changes were made in Sections 2 and 4 and footnotes were renumbered in January 1983.

1. Scope

1.1 These methods cover the comparison of petroleum oils recovered from water or beaches with oil from suspect sources by means of gas chromatography (1, 2, 3).[2] Such oils include distillate fuel, lubricating oil, and crude oil. Methods are described for packed and capillary column analyses using either single detection (flame ionization) or dual detection (flame ionization and flame photometric for sulfur).

	Sections
Method A—Packed Column	9 to 17
Method B—Capillary Column	18 to 26

1.2 Method A provides a low-resolution separation; Method B provides a higher resolution for more critical examination. The dual detection scheme should be employed whenever possible. The flame-photometric detection for sulfur compounds is an adjunct, not a substitute, for flame-ionization detection in the identification of waterborne petroleum oils (4 to 12). There are, however, certain circumstances where the sulfur chromatograms can distinguish two oils when the flame ionization chromatograms cannot.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1129 Definitions of Terms Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2549 Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography[4]

D 3415 Practice for Identification of Waterborne Oils[4]

D 3325 Practice for Preservation of Waterborne Oil Samples[4]

D 3326 Practice for Preparation of Sample Identification of Waterborne Oils[4]

D 3327 Methods for Analysis for Selected Elements in Waterborne Oils[4]

E 260 Practice for General Gas Chromatography Procedures[5]

E 355 Practice for Gas Chromatography Terms and Relationships[5]

3. Significance

3.1 Identification of a recovered oil is determined by comparison with known oils, selected because of their possible relationship to the particular recovered oil. The known oils are collected from suspected sources. Samples of such known oils must be collected and submitted along with the unknown for analysis. At present, identification of the source of an unknown oil by itself cannot be made (for example, from a library of known oils).

3.2 The use of a flame-photometric detector in addition to the flame-ionization detec-

[1] These methods are under the jurisdiction of ASTM Committee D-19 on Water.

Current edition approved Jan. 27, 1978. Published April 1978. Originally published as D 3328 – 76b T. Last previous edition D 3328 – 76a T.

[2] The boldface numbers in parentheses refer to the references at the end of these methods.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 11.02.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

tor provides a second, independent profile of the same oil, that is, significantly more information is available from a single analysis with dual detection.

3.3 Many close similarities (within uncertainties of sampling and analysis) will be needed to establish identity beyond a reasonable doubt. The analyses described will distinguish many, but not all samples. For cases in which this method does not clearly identify a pair of samples, and for important cases where additional comparisons are needed to strengthen conclusions, other analyses will be required, such as Method B, and other appropriate methods (Practice D 3415, 4.6).

3.4 For Method B, the "deasphalted" fraction of neat petroleum or petroleum residue is prepared to provide a sample free of asphaltenes in order to protect the capillary column.

4. Definitions

4.1 For definitions of terms used in these methods, refer to Practice D 3415, Definitions D 1129, and Recommended Practice E 355.

5. Interferences

5.1 Compounds that have the same retention time as petroleum hydrocarbons will interfere in the comparison of the unknown with known oils. This is particularly true if animal fat or vegetable oil, naturally occurring hydrocarbons, or spill-treatment chemicals are present in relatively large amounts. Independent analysis, for example, infrared spectroscopy, will establish the presence of these contaminants if their presence is suspected. Animal or vegetable oils can be removed effectively by Method D 2549 or by Practice D 3326 (Method D).

NOTE 1—Method D 2549 will also remove the aromatic fraction.

6. Reagents and Materials

6.1 *Purity of Reagents*—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.[6]

6.2 Unless otherwise indicated references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II.

6.3 *Air*—For use with the flame-ionization and flame-photometric detectors; may be obtained using a laboratory pure air generator, or from a zero grade tank supply.

6.4 *Carrier Gas*—High-purity grade helium is used as carrier gas.

6.5 *Cyclohexane*—For use in reference standards.

6.6 *Hydrogen*—For use with the flame-ionization and flame-photometric detectors; may be obtained using a hydrogen generator, or from a prepurified grade tank supply.

6.7 *Methylene Chloride*—For use in reference standards and glassware cleaning.

6.8 *Normal Alkane Standards*—Normal alkanes, decane through hexatriacontane, for use as reference compounds.

6.9 *Normal Pentane*—Chromato-quality, normal pentane is used for sample deasphalting.

6.10 *Thiophene*—For use in optimization of flame-photometric detector.

7. Reference Standards

7.1 *Normal Paraffinic Hydrocarbons*—Prepared mixtures of approximately decane to hexatriacontane, or selected individual normal paraffins, are run under normal analysis conditions to determine retention times of compounds.

7.2 *Resolution Mixture*—Equal mixtures of *n*-hexadecane, *n*-octadecane and eicosane in cyclohexane solution (100 µl of each diluted to 10 ml with cyclohexane). See the annex for details (see A1.2.1).

8. Sampling

8.1 Collect a representative sample. The method used depends upon the quantity of sample available. If only a thin sheen is present on the water, the oil can be picked up by dipping TFE-fluorocarbon strips (50 by 75 by 0.25 mm). The adhering properties of the TFE-fluorocarbons can be enhanced by roughing (etching) the surface, or by perforating with 1.6-mm holes (5/cm²). The TFE-fluorocarbon strips are placed in a solvent-rinsed glass jar and sealed with TFE-fluorocarbon or aluminum-lined cap to avoid plasticizer contamination.

8.2 If the sample is not to be analyzed within 1 week, it should be preserved in accordance with Method D 3325 because of the possibility of bacterial decomposition of normal paraffins in the sample.

8.3 The sample should be prepared for analysis in accordance with Practices D 3326, because of the great variety of materials and circumstances associated with collecting petroleum oils from the environment. This preparation procedure removes water, particulate matter and asphaltenes (high molecular weight components that would build up on the column and effectively shorten its useful life).

METHOD A—PACKED COLUMN PROCEDURE

9. Scope

9.1 This method is applicable to samples of neat petroleum, or to prepared petroleum residue.

10. Summary of Method

10.1 This method uses a gas chromatographic packed column system for the separation of petroleum hydrocarbons. The effluent of the column may be detected with a flame-ionization detector, or it may be split (1+2) between a flame ionization and a flame-photometric detector. The flame photometric detector is equipped with a narrow bandpass interference filter for spectral isolation of the sulfur emission at 394 nm. The relative peak size of each component (as indicated by retention time) of recovered oil is compared visually with the relative peak size of each component (of like retention time) of the suspected source. A discussion of gas chromatography is presented in Recommended Practice E 260.

NOTE 2—This dual detector method is based on the early work done by Kahn (13), Garza (4), and Adlard (7). Kahn and Garza currently use a method that does not employ an effluent split for simultaneous dual detection.

10.2 In this method, elution of characteristic hydrocarbons occurs generally in order of increasing boiling point.

11. Apparatus

11.1 *Chromatographic Column*—Columns may be purchased or prepared by the analyst.

11.1.1 *OV-101*[7]—A ⅛-in. by 10-ft (3-mm by 3-m) stainless steel column with 0.012-in. (0.3-mm) wall, packed with 60/80 mesh Chromosorb W[8] (acid washed and dimethylchlorosilane (AW-DMCS)-treated) coated with 10 weight % of OV-101.

11.2 *Gas Chromatograph*—A commercial or custom designed gas chromatograph with heated injection and detector zones and a column oven capable of being programmed from 75°C to at least 325°C for heavier oils (higher boiling than gasolines, jet fuels, etc.).

11.2.1 For light distillate fuels, the chromatograph must be capable of programming from 50°C and also be capable of maintaining isothermal control at 50°C.

11.2.2 *Injection Port*—The use of glass injector inserts that can be replaced or cleaned frequently, or both, will prolong the useful life of the column (3).

11.2.3 *Detectors*—A hydrogen-flame ionization detector is always used for Method A. In addition a flame-photometric detector with a 394 nm bandpass filter is used for dual detection (9, 10, 11, 12).[9,10]

11.2.4 *Effluent Splitter*—An effluent splitter with a split ratio of 1+2 (FID/FPD) is required for dual detection.

11.2.5 *Blender for Reference Compound*—A device for in-line blend of a reference compound (thiophene and cyclohexane) into the carrier flow for detector optimization is

[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopeia."

[7] A registered trademark of Ohio Valley Specialty Chemical Co.

[8] A registered trademark of Johns-Manville Products Corp.

[9] The flame-photometric detector nearly universally used is that developed by Melpar and marketed under license by MetroTec Instrument Corp. of Austin, Tex.

[10] Flame-photometric detector with fiber optics were developed by Tosh Bendix and Perkin-Elmer. They are currently available from Perkin-Elmer, Norwalk, Conn. Fiber optics permit removal of the photomultiplier tube from the heated flame zone which in turn permits operating temperatures of up to 450°C (versus the usual 250°C).

required, when using a flame-photometric detector.

11.2.6 *Strip-Chart Recorder*—A strip-chart recorder is required to measure detector response at full-scale range of 1 mV with a response time of 1 s (or less). A second recorder, or dual-pen recorder is required for dual detection.

11.3 *Syringe*—A microsyringe of 0.5 to 1 µl capacity.

11.4 *Gas Traps*—Any commercially available gas filter traps to be placed in line to remove trace hydrocarbon and water impurities from the helium, hydrogen, nitrogen, and air gas supplies.

11.5 *FPD Linearizer*—Optional accessory to facilitate comparison of FPD chromatograms.

12. Preparation of Chromatograph

12.1 Install the column in the chromatograph.

12.2 Shut off the downstream end of the system and pressurize the carrier gas supply to a gage pressure of approximately 15 psi (103 kPa) above the operating pressure. Shut off the cylinder valve and observe the pressure gage. Consider the system tight if no pressure drop is noted in 10 to 15 min. Use a small amount of aqueous soap solution to locate minor leaks. Do not use the soap solution near the ionization detector.

12.3 *Column Conditioning for New Columns*

Note 3—For previously conditioned columns, proceed to 12.3.5.

12.3.1 Disconnect the column at the detector end to avoid deposition of volatiles on the detector(s) during conditioning.

12.3.2 For freshly prepared columns, pass helium through and cap the column with a brass or stainless steel plug. Program the oven to 325°C and hold for 4 h. Cool and remove the plug. For older columns, proceed directly with Step 12.3.5.

12.3.3 Adjust the carrier gas flow as indicated in Table 1.

12.3.4 Raise the column temperature to 275°C and hold at this temperature for 1 h with normal carrier flow rate.

12.3.5 Increase the column temperature to 300°C and hold at this temperature for at least 1 h with normal carrier flow.

12.3.6 Increase the column temperature to 325°C and hold overnight with the normal carrier flow rate.

12.3.7 Heat to 350°C and hold for ½ h.

12.3.8 After conditioning, cool the column and connect it to the detector(s).

12.3.9 Adjust the hydrogen and air flow, and the air/hydrogen flow ratio to the detector(s), as specified for the instrument being used. Ignite the flame(s) (see 12.4 for optimization).

12.3.10 Adjust the carrier gas flow as indicated in Table 1.

12.3.11 Program the column temperature as indicated in Table 1, and hold at the maximum temperature while monitoring the effluent. If there are no peaks in the chromatogram and there is minimal baseline shift at high temperatures, then the column is ready for use; otherwise recondition it.

12.3.12 Return the oven temperature to 75°C.

12.3.13 If the column is to be moved or stored, disconnect and seal the ends of the column. When the column is to be reused, even after conditioning, it is always necessary to cycle through the temperature program to remove any accumulated volatiles.

12.4 *Optimization of Detectors*—Adjust hydrogen and air flows to give optimal detector responses for a given background sample signal provided by the reference compound blender (13.2.5). Use cyclohexane for FID optimization and thiophene for the FDP optimization.

13. Operating Conditions for Analysis (Notes 4, 5, 6)

Note 4—One of the problems frequently encountered with the flame photometric detector is "flameout" when large amounts of solvent are injected with the sample. The recommended sample preparation procedure avoids this problem at the same time that it permits the use of small samples. For those who may encounter this problem, a simple modification has been suggested (8) which consists of reversing the hydrogen gas and air/oxygen gas inlets to the detector.

Note 5—For all identifications under the recommended procedure, air has been found satisfactory for combustion for the FPD, that is, oxygen is not necessary.

Note 6—See the manufacturer's manual for maintenance information for the FPD. Present flame photometric units should not be heated above 350°C, unless the photometer is removed from the heated zone by fiber optics; older units cannot be heated above 170°C. Periodically, it may be necessary to remove the flame jet and clean it with solvent (cyclohexane) in an ultrasonic bath.

13.1 Operating conditions are summarized in Table 1; apparatus operated under these conditions should achieve partial resolution of two pairs of normal and isoprenoid hydrocarbons found in many, but not all, crude oils and certain petroleum products. In order of emergence from the column, these are heptadecane and pristane, and octadecane and phytene.

13.1.1 Each day, analyze the resolution mixture to test the column performance, monitor the instrument performance and thermally equilibrate the system (see the *Annex* for details).

13.1.2 Apply annex procedure to ensure that column performance is acceptable. Repeated injection of samples containing asphaltenes will change the resolving power of the column until the column eventually will degrade to the point where its performance is no longer acceptable.

14. Component Identification

14.1 In most instances, it is unnecessary to identify individual components when comparing chromatograms of a split with its source; it is sufficient to note their degree of match. Identification of the usually dominant normal paraffin hydrocarbons is readily achieved by comparing their retention times with those from known n-alkane standards.

14.1.1 Identification of peaks other than normal paraffins is not achieved, except in rare cases.

14.1.2 Comparison of peaks with the same retention times in the known and unknown oils is also made with respect to relative peak sizes of adjacent peaks.

14.2 To determine the retention time of normal paraffins, the following procedure is recommended:

14.2.1 With the column at the initial operating temperature, inject 0.2 µl of the known mixture of normal paraffins (11.1).

14.2.2 Turn on the recorder and mark the injection point on the recorder chart.

14.2.3 Adjust the instrument attenuation so that the maximum peak heights are on scale.

14.2.4 When the temperature program is complete and the baseline has stabilized, cool the oven to the initial temperature.

14.2.5 Measure the retention time in minutes to at least two significant figures for each normal paraffin in the known mixture.

15. Procedure for a Sample

15.1 First, cycle the instrument through its program to test the column and instrument performance (13.1) and thermally equilibrate the oven.

15.2 Zero the strip-chart recorder pen and make appropriate notations at the beginning of the chromatogram (sample name, reference number, date, amplifier attenuations).

15.3 For light distillate oils (such as gasoline, jet fuels, kerosines, and No. 2 fuel oils), inject 0.2 µl of sample directly into the injection port with the column at initial operating temperature. For heavier oils, deasphalt with 15 parts of pentane, before injecting the 0.2-µl sample (after pentane removal).

15.4 Start the recorder and the temperature program. Mark the injection point on the recorder chart.

15.5 Adjust the attenuations so that the highest peak is retained on scale and constant baselines are achieved after the analysis. Obtain a complete chromatogram at a single attenuation, repeating if necessary until a satisfactory chromatogram is obtained.

15.6 When the temperature program is complete and the baseline has stabilized, cool the oven to the initial temperature. (This is automatic for most instruments.) After resetting the initial conditions, another sample may be analyzed.

15.7 After completion of the analysis, record the following information for each set of chromatograms: column length and diameter; liquid phase and weight percent; support material and mesh size; initial and final column temperatures; programming rate; carrier gas flow rate; detector manifold and injection port temperatures; FPD heater temperature (if used); hydrogen and air flow rates; injection port split ratio and effluent split ratio (if employed); sample size and amplifier ranges. (Rubber stamps are commercially available which facilitate the recording of these data.)

15.8 Prepare chromatograms of samples of known origin, that is, from potential sources

(see 15.1 to 15.7).

16. Interpretation

16.1 *Basis of Matching*—The matching of oil samples is essentially a profiling technique based on the premise that identical oils give identical chromatograms. Normally, the matching of a spilled oil to a suspect oil can be accomplished by comparison of the chromatograms for each of the oils in a spill case.

16.2 *Chromatogram Features*—The major features of a chromatogram used for comparison are listed as follows and are illustrated in Figs. 1 and 2 (gas chromatograms of a Kuwait crude oil which depict FID as well as PFD curves).

16.2.1 The FID curve shows a typical separation with the features of a homologous series of normal paraffins, the isoprenoid hydrocarbons pristane and phytane, the unresolved envelope and other resolved peaks. All of these features are used to characterize an oil.

16.2.2 The PFD curve has fewer readily ascribed characteristics; rather it gives the overall sulfur profile generated by the detector. It is useful not only qualitatively, but semiquantitatively.

16.3 *Weathering Effects:*

16.3.1 When an oil is spilled on open water, or a relatively small amount of oil is widely dispersed in an area such as a bilge tank, weathering will progress rapidly. A thin slick on open water may lose significant amounts of its components up to *n*-C_{15} (271°C atmospheric boiling point) within 48 h of being spilled. It is important to be cognizant of the effects of weathering when analyzing spill samples more than a few hours old. It is advisable to compare only those portions of chromatograms boiling above pentadecane in order to minimize the difference resulting from changes due to weathering.

16.3.2 Light distillate fuels cannot survive heavy weathering and have few hydrocarbons above C_{10}. Comparison of the residues of these oils can only be done qualitatively—from about C_8–C_{10}.

16.4 *Comparison of Chromatograms:*

16.4.1 Normally a direct comparison of chromatograms, considering the features enumerated above, will suffice for establishing identity or nonidentity between samples. The comparison involves simply a peak-for-peak matching, noting differences or similarities in relative peak size. If the chromatograms are the same on the basis of peak-for-peak matching, there is a high degree of probability that the samples are from the same source. A mismatch is obtained when the curves are different. The differences may be due to the presence of one or more components in one sample relative to another or consistent differences in relative intensities of peak responses, or both. Spill samples may contain components such as bilge cleaning detergents, plasticizers, paint vehicles, etc. The presence of one or two components in a spill sample, which are absent in a suspect, is not intrinsically indicative of nonidentity.

17. Report

17.1 Based upon the visual comparison of chromatograms, and after considering 8.2, 16.3, and 1.5.4, report the sample of unknown origin as belonging to one of the categories below:

17.1.1 *Match*—Like one, or more, of the samples submitted for comparison.

17.1.2 *Probable Match*—Like one, or more, of the samples submitted for comparison, except: (*a*) for changes which could be attributed to weathering (specific low molecular weight peak losses), or (*b*) differences attributable to specific contamination.

17.1.3 *Indeterminate*—Like one, or more, of the samples submitted for comparison, except for certain differences as in 17.1.2 of such magnitude that it is impossible to ascertain whether the unknown is the same oil heavily weathered, or a totally different oil.

17.1.4 *Mismatch*—Unlike the samples submitted for comparison.

METHOD B—CAPILLARY COLUMN PROCEDURE

18. Scope

18.1 See Section 9, but using a capillary column procedure.

19. Summary of Method

19.1 This method makes use of a gas chromatographic capillary column system for separation of petroleum hydrocarbons and either FID or FID and PFD for their measurement. The relative peak size of each component (as indicated by retention time) from a spill sample is compared with the relative peak size of each component (of like retention time) of a similarly prepared sample from the suspected source. Thus, Method B is basically the same as Method A except for the use of a higher resolution column.

20. Apparatus

20.1 *Chromatographic Column* (see 11.1):

20.1.1 *OV-101*[3]—A 0.02-in. by 50-ft (0.5-mm by 16-m) support coated open tubular (SCOT) stainless steel column.

20.2 *Gas Chromatograph* (see 11.2)—The same gas chromatograph used in Method A may be used in Method B provided it has the necessary fittings to accommodate the capillary column and:

20.2.1 *Carrier Gas Pressure Regulator* is substituted pressure regulator for the mass flow controllers to give more precise flow rates in the low flow ranges (1 to 5 ml/min).

20.2.2 *Effluent Splitter* is required for the column effluent, with a split ratio of 1 + 2 FID/FPD.

20.2.3 *Carrier Gas Makeup* is required at the effluent end of the column with a temperature-independent mass flow controller.

20.3 *Detectors*—A hydrogen flame-ionization detector and for dual detection a flame-photometric detector (see 11.2.3).

20.4 *Strip-Chart Recorder* (see 11.3.6).

20.5 *Microsyringe* (see 11.3).

20.6 *Bleeder for Reference Compound* (see 11.2.5).

21. Test Sample (Spilled oil)

21.1 Using 1 to 2 ml of neat petroleum, prepare a sample in accordance with Practice D 3326.

22. Preparation of Chromatograph

22.1 See Section 12.

23. Operating Conditions for Analysis

23.1 Operating conditions are summarized in Table 1.

NOTE 7—See A1.3.1 for the results expected on a new, properly conditioned SCOT column. A properly functioning column should provide 400 to 600 analyses, depending on the type of oil analyzed.

24. Method of Comparison

24.1 As instructed in Sections 14 and 16.

25. Procedure for a Sample

25.1 With the column at initial operating temperature, inject a 0.2-µl sample into the injection port.

25.2 See 15.4.

25.3 See 15.5.

25.4 See 15.6.

25.5 See 15.7.

25.6 Prepare chromatograms from samples of known origin in the manner described in 15.6 to 15.7.

26. Report

26.1 Based upon the visual comparison of chromatograms and after considering 3.2 and Section 16, report the sample of unknown origin as belonging to one of the categories below:

26.1.1 *Match* (see 17.1.1).

26.1.2 *Probable Match* (see 17.1.2).

26.1.3 *Indeterminate* (see 17.1.3).

26.1.4 *Mismatch* (see 17.1.4).

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(13) Kahn, L., McKown, G. F., and Cooper, L., "Characterization and Identification of Oils Obtained from the Environment," presented at the 159th National ACS Meeting, Houston, February 1970.

TABLE I Operating Conditions for Chromatographic Columns (11, 12, 13)

	Method A	Method B
Column	¼-in. by 10-ft (3-mm by 3-m) stainless steel (see 11.1.1)	0.02-in. by 30-ft (0.5-mm by 10-m) stainless steel (see 20.1.1)
Packing	10 % OV-210[a], 80/90 mesh Chromosorb W (AW-DMCS)	OV-101 SCOT
Carrier gas	helium	helium
Flow, ml/min		
Column	approximately 30	approximately 2
Makeup gas	none	approximately 30
Temperature, °C		
Injection port	300	250
Column:		
Starting edit		
Initial	75	75
Final	315 (FID) 250 (FID/FPD)	250 (FID) 250 (FID/FPD)
Ramp edit		
Initial	50 hold 2 min	50 hold 2 min
Final	250	250
Detector	350 (FID) 250 (FID/FPD)	275 (FID) 250 (FID/FPD)
Program Rate	8-10[a]	6-8[a]
Chart speed, inch (mm/min)	2.5 (10)	2.5 (10)
Sensitivity, mV	1	1
Sample size, µl	0.2	0.2
Effluent split ratio (FPD procedure)	1+2 (FID/FPD)	1+2 (FID/FPD)

[a] The precise rate is dictated by the design of the gas chromatograph.

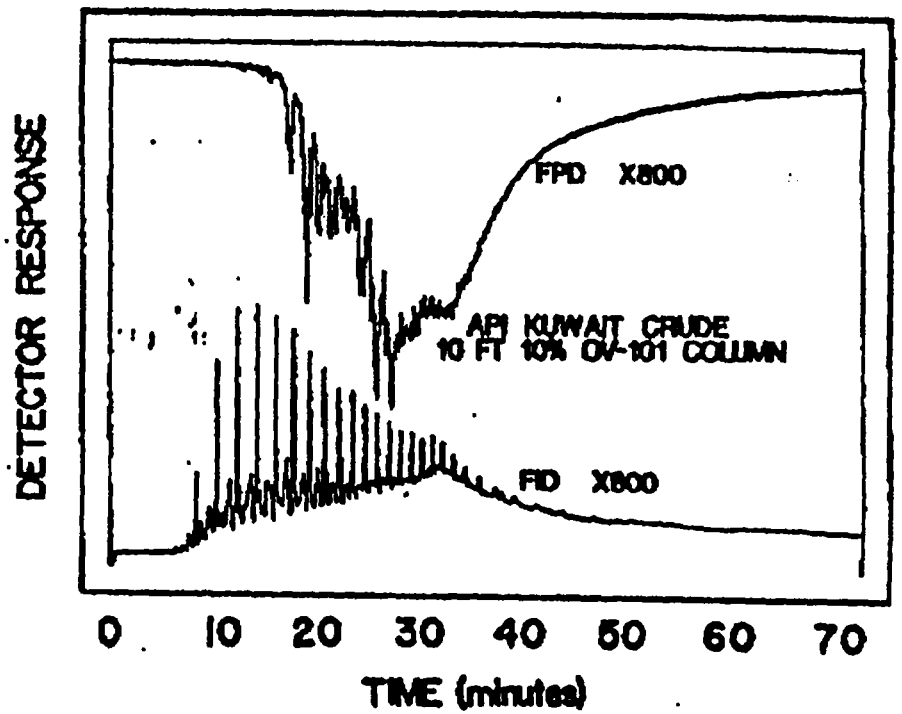


FIG. 1 Representative Chromatograms from Packed Columns (Methods A1 and A2).

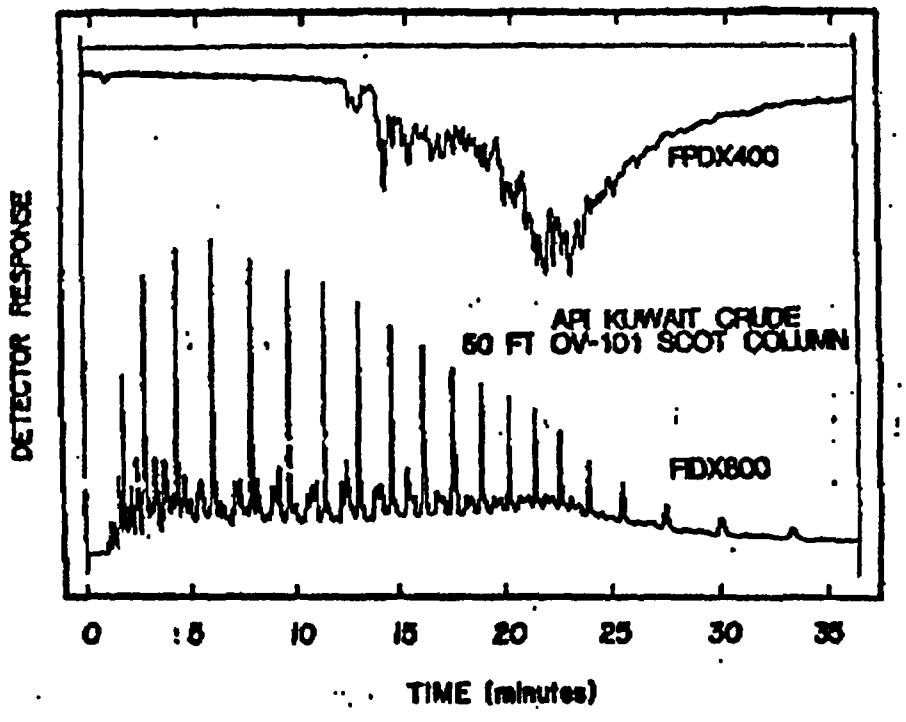


FIG. 8 Representative Chromatograms from Capillary Columns (Methods B1 and B2).

ANNEX

A1. COLUMNS

A1.1 Column Performance

A1.1.1 The level of performance of the chromatographic system, in particular the gas chromatographic column, can be quantitated by calculation of the resolution of specific components. The term "resolution" is defined in Recommended Practice E 355. The resolution values for normal alkanes are used in defining column performance for this recommended practice.

A1.2 Procedure

A1.2.1 A resolution mixture is prepared consisting of 100 µl each of normal alkanes n-C16, n-C18, and n-C20; the alkanes are dissolved in cyclohexane in 10-ml volume. Gentle warming of the solution may be necessary to carry out their transfer. The solution is prepared in a 10-ml volumetric flask.

A1.2.2 Instrumental conditions, gas flows, and temperature programming are exactly the same as for the analysis of samples (see Section 12). A 0.2-µl injection volume is used for analysis and will give a 35 to 60 % full-scale recorder response at normal amplifier settings used for oil samples. The resultant peaks are of the approximate size of the same peaks that will be found for many oil samples. Examples of the resolution mixture for packed and SCOT column operation are shown in Fig. A1.1 and A1.2, respectively.

A1.2.3 The resolution for the peak pairs n-C16 and n-C18 and for n-C18 and n-C20 are determined using Recommended Practice E 355.

NOTE A1—A faster chart speed of 180 to 200 mm/min will improve the measurement of peak width. The measurement of peak width at half height may be necessary when peak tailing occurs; this measurement should be doubled for use in resolution equations.

A1.3 Performance Standards

A1.3.1 The resolution of components for a well performing column will give resolution values for packed columns of Sections 13 and 14, and for SCOT

column values of 23 and 20 for the peak pairs n-C16 and n-C18 and for n-C18 and n-C20.

A1.3.2 Columns should be replaced and operating conditions thoroughly checked should resolution values approach 75 % of the values in A1.3.1.

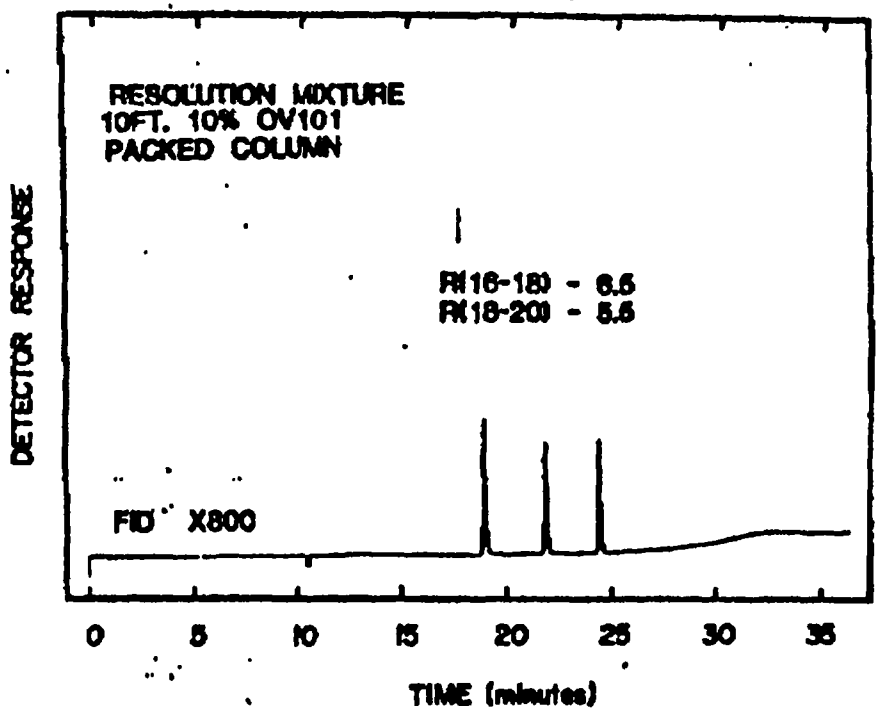


FIG. A1.1 Resolution on Packed Column.

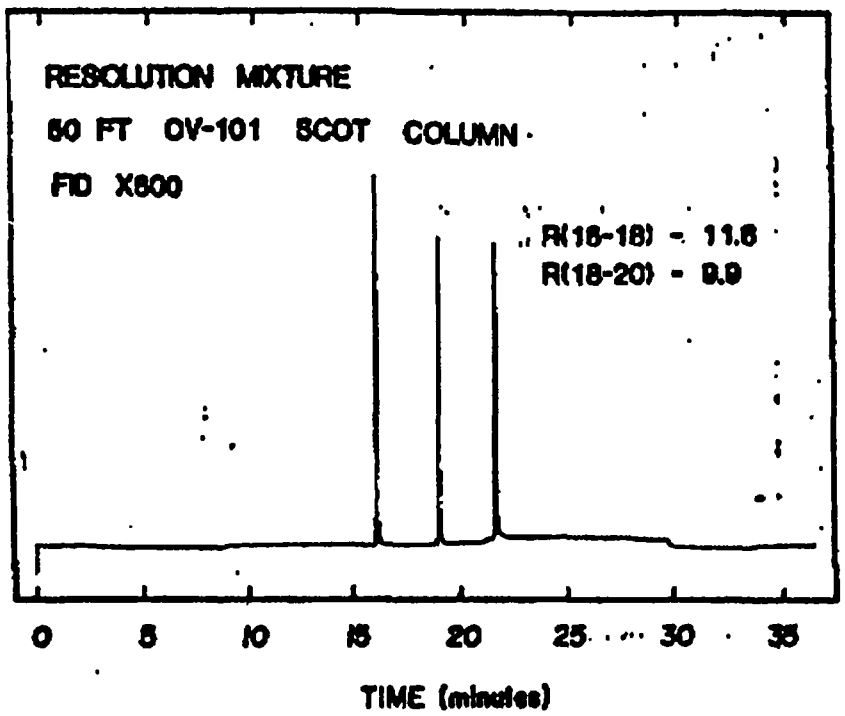


FIG. A1.3 Resolution on Capillary Column.

Designation: D 3650 – 78 (Reapproved 1982)[1]

Standard Method for COMPARISON OF WATERBORNE PETROLEUM OILS BY FLUORESCENCE ANALYSIS[2]

This standard is issued under the fixed designation D 3650; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

[2] Note – Editorial changes were made in Sections 2 and 3 and footnotes were renumbered in January 1983.

1. Scope

1.1 This method covers the comparison of waterborne petroleum oils with oils from possible sources by means of fluorescence spectroscopy (1).[3] Useful references for this method include: (2) and (3) for fluorescence analysis in general and (4), (5), and (6) for oil spill identification including fluorescence.

1.2 This method is applicable to crude or refined petroleum products, for any sample of neat oil, waterborne oil, or sample of oil-soaked material. Unless the samples are collected soon after the a spill occurs, it is not recommended that volatile fuels such as gasoline, kerosine, and No. 1 fuel oils be analyzed by this method, because their fluorescence signatures change rapidly with weathering. Some No. 2 fuel oils and light crude oils may only be identifiable up to 2 days weathering, or less, depending on the severity of weathering. In general, samples weathered up to 1 week may be identified, although longer periods of weathering may be tolerated for heavy residual oils, oil weathered under Arctic conditions, or oil that has been protected from weathering by collecting in a thick layer.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1129 Definitions of Terms Relating to Water[4]

D 1193 Specification for Reagent Water[4]

D 1796 Test Method for Determination of Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)[5]

D 3325 Practice for Preservation of Waterborne Oil Samples[6]

D 3326 Practices for Preparation of Samples for Identification of Waterborne Oils[6]

D 3328 Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography[6]

D 3414 Methods for Comparison of Waterborne Oils by Infrared Spectroscopy[6]

D 3415 Practice for Identification of Waterborne Oils[6]

E 131 Definitions of Terms and Symbols Relating to Molecular Spectroscopy[7]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[8]

E 578 Recommended Practice for Describing Detectors in Emission and Absorption Spectroscopy[7]

2. Summary of Method

2.1 This method consists of fluorescence analyses of dilute solutions of oil in spectroquality cyclohexane. In most cases the emission spectra, with excitation at 254 nm, over the spectral range from 280 to 500 nm, are adequate for matching.

[1] This method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.10 on Identification of Waterborne Oils.

Current edition approved Jan. 27, 1978. Published April 1978.

[2] The boldface numbers in parentheses refer to the references at the end of this method.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vol 11.02.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

[7] *Annual Book of ASTM Standards*, Vol 03.06.

APPENDIX G
ANALYTICAL METHOD FOR DETERMINING FUEL OIL COMPONENT IN SOIL/SEDIMENT

Subject or Title: Total PAH and/or Total Petroleum Hydrocarbons in Soils (Modified ASTM Method 3328-78)

SOP No.:	Revision No.:	Effective Date:
LM-ERC-4602.1	1.0	Sept. 25, 1990

1. Scope and Application

1.1 Polynuclear Aromatic Hydrocarbons (PAH)

1.1.1 PAH Analytes - Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, 1-methylnaphthalene, and 2-methylnaphthalene.

1.1.2 Detection limits - The method detection limit for a 30-g sample is 200 µg/kg (dry weight) for resolved PAH components.

1.1.3 Applicable matrices - Sediment and soil samples.

1.1.4 Dynamic range - 200 µg/kg to 3,000 µg/kg (120 ng on column).

1.1.5 Approximate analytical time - Gas chromatography (GC) analysis takes 2.0 hours and is automated.

1.2 Petroleum Hydrocarbons

1.2.1 Petroleum Analytes - Gasoline, kerosene, paint thinner, turpentine, Fuel Oil No. 2, Fuel Oil No. 4, Fuel Oil No. 6, coal tar, creosote, lubricating oils, leaf hydrocarbons, processing oils, and asphalt.

1.2.2 Detection limits - The method detection limits for a 30-g sample are 0.25 µg/g for resolved components and 10 µg/g for total products.

1.2.3 Applicable matrix - Soil samples.

1.2.4 Dynamic range - 10 µg/g to 1,000 µg/g for the total product.

1.2.5 Approximate analytical time - Gas chromatography (GC) analysis takes 1.5 hours and is automated.

Prepared by: Thomas R. Copeland, Ph.D.	Date: Sept.25, 1990
Management Approval:	Date:
QA Officer Approval:	Date:

2. Summary of Method

A measured mass of sample (approximately 30 g - wet weight) is mixed with sodium sulfate, spiked with an ortho-terphenyl (OTP) internal standard, and soxhlet-extracted (EPA Method 3540, appendix 1). The methylene chloride extract is dried and concentrated to 1 mL or less by rotary evaporation. Deuterated internal standards are added to each extract and 1-2 μL of each extract is injected onto a capillary gas chromatograph/flame ionization detector (GC/FID). Instrument conditions are described that permit the separation and semiquantitative measurement of the 16 priority pollutant polynuclear aromatic hydrocarbon (PAH) compounds. Total petroleum hydrocarbon concentration and qualitative petroleum product identification are also possible using this method. Androstane (a GC standard) is added to each extract and 1-2 μL of each extract is injected onto the capillary gas chromatograph/flame ionization detector (GC/FID). The method is intended to afford petroleum product identification and quantitation and semiquantitative analysis of PAHs.

3. Comments

3.1 Interferences

3.1.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Reagent blanks must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

3.1.2 High purity reagents such as Burdick and Jackson GC[2] methylene chloride or Baker capillary grade methylene chloride must be used to minimize interference problems.

3.1.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure (EPA Method 3630) can be used to overcome many of these interferences, but is not necessary with the site specific analytes of interest.

3.1.4 Petroleum hydrocarbon products contain PAH compounds and PAH contaminants are formed from the use of petroleum hydrocarbon products. Proper interpretation of the results requires an experienced analyst.

3.1.5 Presence of a large excess of a petroleum product will prevent quantitation of coeluting PAHs.

4. Safety Issues

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for use by the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known, suspected, human, or mammalian carcinogens. They are benzo(a)anthracene, benzo(a)pyrene, and dibenzo(a,h)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene.

5. Sample Collection, Preservation, Containers, and Holding Times

5.1 Sample collection - Soil samples should be collected with solvent-rinsed stainless steel spatulas and placed in solvent-rinsed aluminum foil-lined 8-oz wide-mouth jars.

5.2 Sample preservation - Samples are placed on ice immediately after collection and refrigerated at 4°C until the time of analysis.

5.3 Sample container - Samples are stored in prewashed and solvent-rinsed 8-oz wide-mouth jars with aluminum foil-lined lids.

5.4 Holding times - The sample holding time is ~~14~~ 10 days after sample collection.

6. Apparatus

6.1 The following glassware is used for this method.

- 8-oz wide-mouth jars with aluminum foil-lined lids.
- Soxhlet setup.
- Rotary evaporation setup - Buckler Flash Evaporation.
- Vials - 1-mL amber glass vials with Teflon-lined cap, 7-mL vials.
- Glass funnels.
- 500-mL round-bottom flasks.
- Nitrogen blowdown setup.

6.2 An analytical balance capable of accurately weighing 0.001 g should be used.

6.3 An HP 5880A or HP 5890A GC with a split/splitless injector equipped with a capillary column and an FID should be used. The output is connected to a Bechman CALS data acquisition system for the measurement of peak areas.

6.3.1 Column - 30 mm long x 0.32 mm I.D. capillary DB5 column (J&W Scientific Catalog No. 123-5032). This column will allow for the resolution of the deuterated internal standards as well as benzo(b)fluoranthene and benzo(k)fluoranthene.

6.3.2 FID - This detector has proven effective in the analyses of soil samples for the 16 priority pollutant PAH compounds and Total Petroleum Hydrocarbons.

6.3.3 Autosampler - HP 7671 or HP 7673A

7. Reagents and Standards

7.1 Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest.

7.2 Methylene chloride, hexane - pesticide or equivalent.

7.3 Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.4 Silica gel - Grade 923 (100/200) dessicant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil.

7.5 Standards

7.5.1 Prepare standards of the 16 priority pollutants from the Supelco Supelpreme-HC PAH mix (Catalog No. 4-8905) at 10 ng/μL, 20 ng/μL, 40 ng/μL, 60 ng/μL, and 120 ng/μL in methylene chloride. Prepare qualitative standards of the Fuel Oil #2 at 2-5 mg product/mL methylene chloride. All standards are validated by a concentration check for chromatographic purity using a standard prepared at a different time or obtained from a different source. Protect all PAH standards from excessive exposure to light.

7.5.2 Internal standards (IS) are prepared by carefully weighing out 200 mg of D_8-naphthalene, D_{10}-acenaphthene, D_{10}-phenanthrene, D_{12}-perylene, OTP, and 5α-androstane and adding these compounds to 50 mL of 10% benzene/90% methylene chloride. Warm solution until all of the D_{12}-perylene dissolves and transfer 5 1-mL aliquots into 1-mL screw cap vials. Warm each 1-mL vial until all of the D_{12}-perylene is dissolved prior to adding 10 μL to the sample extract. Mark each vial with a pen after each use and discard IS at 0.5 mL. Confirm the concentration with GC/MS group standards and Supelco standards.

8. Procedure

8.1 Sample Preparation

8.1.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Remove 5 g of the sample and place it in a preweighed aluminum pan. Dry it at 55°C for 12 hours and calculate the percent solid content.

8.1.2 Weigh out 30 g (wet weight) of the sample. Mix in 30 g of sodium sulfate. If the sample has excessive moisture, add additional amounts of sodium sulfate.

8.1.3 Soxhlet extraction

8.1.3.1 Extract sample with soxhlet extraction according to EPA Method 3540 in SW-846, volume 3. The solid sample is placed in an extraction thimble or between two plugs of glass wool, and extracted using methylene chloride for 16 hours.

8.1.3.2 The soil sample may also be extracted via the Teflon shaker technique if a fingerprint analysis is all that is required on the extract.

8.1.4 Concentrate the methylene chloride extract on a Buchler flash evaporator with the water bath temperature set at 40°C. Concentrate to approximately 4 mL and transfer extract to a 7-mL vial. Rinse the round-bottom flask with 1 mL of $MeCl_2$ and transfer the rinseate to 7-mL vial. Blowdown extract to <1 mL with nitrogen. Adjust extract volume to 1 mL with methylene chloride.

8.1.5 Add 10 µL of IS to each extract.

8.2 Calibration

8.2.1 For PAHs, calibrate each GC with an initial five-point calibration curve. The lowest concentration point in the calibration curve should be near the MDL. The highest concentration point should be twice the expected sample concentration and within the linear instrument range. In addition, analyze a 1000 µg/kg site specific coal tar standard.

8.2.2 For TPHs, calibrate each GC with an initial three-point (i.e., 10 ng/µL, 50 ng/µL, and 100 ng/µL) calibration curve. The lowest concentration point in the calibration curve should be near the MDL. The highest concentration point should be twice the expected sample concentration and within the linear instrument range. The calibration compounds are decane, acenaphthene, ortho-terphenyl, androstane, eicosane, pyrene, berzo(b)fluoranthene, and triacontane. The relative standard deviation (RSD) of the calibration compound's relative response factors (RRF) must be less than ±15%.

8.2.3 With each day's run, open a 24-hour analyses window. This is done by running a midrange standard containing the 16 priority pollutant compounds plus 10 µL of the IS, 20 µg of OTP, and 20 µg of 5α-androstane and the 8 TPH calibration compounds at 50 ng/µL.

8.2.4 The response factor (Rfs) of each compound should agree with a standard curve Rfs of ±25%. If the Rfs is outside the acceptable limit, the instrument must be recalibrated.

8.2.5 The IS response and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time for the IS changes by more than 30 seconds from the last check calibration (24-hour), the chromatographic system must be inspected for malfunctions and corrections must be made (as is required). If the area for the IS (OTP) changes by ±50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made (as is appropriate).

8.3 Analysis

8.3.1 Samples are analyzed by capillary GC/FID. The column used is a 30 mm x 0.32 mm I.D. DB5 (J&W Scientific Catalog No. 123-5032). The relative standard deviation of responses for replicate injection must be less than 10%.

8.3.2 Refer to appendix 6-2 for standard GC operating parameters.

8.3.3 Inject 1-2 µL of the sample extract using an autosampler device such as a HP 7671A or HP 7673A.

8.3.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

8.3.5 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze it.

8.3.6 If the measurement of the peak response is prevented by the presence of interferences, further cleanup may be required.

8.3.7 Qualitative identification is achieved by direct comparisons of sample chromatograms to the standard product chromatograms. The criteria for matching includes the presence of resolved and unresolved components, product boiling range of the unresolved complex mixture, and any unweathered resolved components that can be used. The accuracy of the interpretation is heavily dependent upon the experience of the analyst.

9. Quality Assurance/Quality Control (QA/QC) Requirements

9.1 QC Samples

9.1.1 A method blank will be analyzed with every batch of less than 20 samples and 1 blank per 20 samples for larger batches (e.g., 2 method blanks for 40 samples).

9.1.2 A blank spike and blank spike duplicate will be analyzed for every 20 samples analyzed. The spiking solution will be prepared at 100 µg/mL methylene chloride and spiked at 0.5 mL into 20 g of sodium sulfate ($NaSO_4$) and 20µL OTP (IS). The spiking compounds are acenaphthene, pyrene, and benzo(a)pyrene.

9.1.3 Sample matrix spikes are analyzed for every 20 samples. If the % recovery is not 60% to 120%, reanalyze both samples. The spiking parameters are found in Appendix 6-2. PAH recovery may be poor if fuel oil is present.

9.1.4 Sample duplicates are analyzed for every 20 samples. If the % difference is > 30%, reanalyze both samples.

9.1.5 Initial calibration correlation coefficients must be >0.99. This criterion must be met before analysis of any samples.

9.1.6 A midrange continuing calibration standard is run once every 20 samples or once every 24 hour analysis window whichever is more frequent. If the % difference is > 15%, recalibrate the instrument and reanalyze all samples analyzed after the last calibration check.

9.2 Acceptance Criteria

9.2.1 Blank levels should be no more than three times the reporting limit.

9.2.2 Blank spike and blank spike duplicate recoveries and QC relative percent differences (RPD) are as follow (from EPA Contract Laboratory Program, 2/88).

Compound	QC-RPD	% Recovery
Acenaphthene	19	31-137
Pyrene	36	35-142
Benzo(a)pyrene	36	35-142

9.2.3 The OTP surrogate recovery criteria is 60-120%.

9.3 Corrective Action Required

When errors, deficiencies, or out-of-control situations exist, the QA program applies systematic procedures (corrective actions) to resolve problems and restore proper functioning to the analytical system. Laboratory personnel are alerted that corrective actions may be necessary if any of the following problems take place.

- QC data are outside the warning or acceptable windows for precision and accuracy.
- Blanks, laboratory control samples, or surrogate control samples contain contaminants above acceptable levels.
- Undesirable trends are detected in spike recoveries or RPD between duplicates.
- There are unusual changes in detection limits.
- Deficiencies are detected by the QA department during internal or external audits, or from the results of performance evaluation samples.
- Inquiries concerning data quality are received from the client.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and so on. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, manager, and/or the QA department for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the QA department. Corrective action documentation is routinely reviewed by the Vice President of QA.

10. Calculations

10.1 The following are lists of IS's and PAH compounds used for calculation purposes.

10.1.1 D_8-Naphthalene

- Naphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene

10.1.2 D_{10}-Acenaphthene

- Acenaphthylene
- Acenaphthene
- Fluorene

10.1.3 D_{10}-Phenanthrene

- Phenanthrene
- Anthracene

10.1.4 5α-Androstane

- Fluoranthene
- Pyrene
- Benzo(a)anthracene
- Chrysene
- Ortho-terphenyl (surrogate) 20 µg/sample

10.1.5 D_{12}-Perylene

- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene
- Benzo(g,h,i)perylene

10.2 The following equations are used for the PAH method.

- $Rfs = (A_s C_{is})/(A_{is} C_s)$

  where:

  A_s = area response of analyte to be measured;
  A_{is} = area response of internal standard;
  C_{is} = concentration of internal standard, µg; and
  C_s = concentration of analyte to be measured, µg.

  Rfs values are calculated from initial daily calibration curve for each PAH compound.

- F = Dilutions/weight of sample (kg).

From sample analysis, determine the area (A_s) of unknown and calculate the concentration.

- $C_s = (A_s C_{is})/(A_{is} R_{fs}) \times F$

10.3 The response factor (RF) of the OTP IS is calculated and used to calculate the TPH concentration.

- $RF = \frac{C_{is}}{A_{is}}$

  where:

  A_{is} = Area response of internal standard (OTP).
  C_{is} = Concentration of internal standard (OTP), µg.

- F = Dilutions/volume of sample.

From sample analysis, determine the total area (A_s) of unknown and calculate the concentration. The analyst must take care when calculating total product areas to be sure that the appropriate baseline is set.

- $C_S = RF \times A_S \times F$

where:

A_S = Area response of analyte to be measured.
C_S = Concentration of analyte to be measured, µg/g (dry weight).

10.4 To determine percent solid content, use the following equation.

$$\% \text{ Solids} = 1 - \frac{\text{Sample wet wt - sample dry wt}}{\text{Sample wet wt - pan weight}} \times 100$$

10.5 Calculation Notes

10.5.1 20 µg OTP surrogate is added to each sample. Percent recovery is calculated using the 5α-androstane (5α-A) IS.

$$\% \text{ OTP recovery} = \frac{A_{OTP} \times C_{5\alpha\text{-}A} \times 100}{A_{5\alpha\text{-}A} \times C_{OTP}}$$

where:

A_{OTP} = area response of OTP;
$A_{5\alpha\text{-}A}$ = area response of 5α-androstane;
C_{OTP} = concentration of OTP; and
$C_{5\alpha\text{-}A}$ = concentration of 5α-androstane.

10.5.2 The RRF calculation for calibration standards is as follows.

$$RRF = \frac{C_{cs} \times A_{is}}{C_{is} \times A_{cs}}$$

where:

C_{cs} = Concentration of calibration standard.
C_{is} = Concentration of internal standard, OTP.
A_{is} = Area of internal standard, OTP.
A_{cs} = Area of calibration standard.

10.5.3 If the D_{12}-perylene Rfs is less than 30% of the average Rfs for D_8-naphthalene, D_{10}-acenaphthene, D_{10}-phenanthrene and 5α-androstane, check the GC for mass discrimination problems.

11. Reporting

11.1 Reporting units - Units are reported in µg/kg dry weight.

11.2 Reporting limits - Reporting limits are 200 µg/kg dry weight for resolved component PAHs. TPH reporting limits are 250µg/kg for individual compounds and 10µg/g (ppm) for total products.

11.3 Significant figures - Significant figures are 2.

11.4 Trace concentrations - Values which are larger than 50% of the reporting limit but less than the reporting limit are noted on the form as trace concentrations.

11.5 Total PAH - To report total PAH, sum the concentrations of all PAH found in the sample.

12. Deliverables

The analytical results shall be presented in a deliverables package which shall, if possible, include the following:

12.1 A case narrative describing the procedure performed by the laboratory and any deviations from the prescribed method. Any problems encountered during analysis and any factors influencing the data must be discussed.

12.2 Chain-of-custody documentation, pertinent telephone logs or telefacsimile transmissions.

12.3 A complete record of internal laboratory daily analytical scheme - run logs or instrument logs including samples, blanks, spikes, etc. in order of analysis.

12.4 The dates of receipt, extraction, and analysis of each sample must be clearly labeled on the data sheets provided.

12.5 Initial calibration results tabulated as in RAS Form VI (EPA/CLP SOW 2/88).

12.6 Continuing calibration results as in RAS Form VII (EPA/CLP SOW 2/88).

12.7 Bench sheets or other documentation showing all sample weights, final extract volumes and dilution factors.

12.8 Spike recoveries, surrogate recoveries and blank results must be provided in tabular form.

12.9 All sample and standard chromatograms, blank chromatograms and QC sample chromatograms must be provided.

13. References

13.1 Method Sources

U.S. Environmental Protection Agency. 1982. "Method 8100," SW-846 - Test methods for evaluating solid waste. Second edition.

American Society for Testing and Materials. "Method D3328-78".

13.2 Deviations from Source Method and Rationale

13.2.1 A Teflon shaker method may be substituted for samples which require fingerprint identification as well as PAH analyses. This preserves the more volatile components in the sample (e.g., gasoline and naphthalene).

13.2.2 A rotary evaporation system is used in place of the Kuderna-Danish (KD) concentration. This system allows for rapid sample concentration without significant loss of the more volatile PAHs (e.g., naphthalene).

APPENDIX 2.
SPECIFIC CONDITIONS FOR TOTAL PAH AND FUEL OIL BY GC

GC CONDITIONS:
Initial column temperature: 40°C.
Initial hold time: 5.0 minutes
Program rate: 3°C/minute
Final column temperature: 300°C
Final hold time: 10 minutes
Injector temperature: 275°C
Detector temperature: 325°C

MATRIX SPIKES AND DUPLICATES:

Samples will be spiked with 16 PAHs, each at 10mg/Kg levels. The compounds are acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, pyrene.

Percent recovery limits and percent difference limits for 3 of these compounds are given in the method. Data regarding the others are not available at this time. It is anticipated that many of these compounds will be subject to interferences due to the presence of high levels of petroleum hydrocarbons in some samples. The spiking level may also be inappropriate for samples found to be heavily contaminated with Site Specific Coal Tar.

METHOD 3540

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor: 40-mm I.D., with 500-mL round-bottom flask.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.7 Glass or paper thimble or glass wool: Contaminant free.

4.8 Heating mantle: Rheostat controlled.

4.9 Syringe: 5-mL.

4.10 Apparatus for determining percent moisture:

4.10.1 Oven: Drying.

4.10.2 Desiccator.

4.10.3 Crucibles: Porcelain.

4.11 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium sulfate: (ACS) Granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hr in a shallow tray).

5.3 Extraction solvents:

5.3.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems.

5.3.1.1 Toluene/Methanol: 10:1 (v/v), pesticide quality or equivalent.

5.3.1.2 Acetone/Hexane: 1:1 (v/v), pesticide quality or equivalent.

5.3.2 Other samples shall be extracted using the following:

5.3.2.1 Methylene chloride: pesticide quality or equivalent.

5.4 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples: Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding: Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (See Method 3500 for details on the surrogate standard and matrix spiking solutions.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place 300 mL of the extraction solvent (Section 5.3) into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask. ROTARY EVAPORATION WILL BE USED FOR ALL PINE STREET SAMPLES.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.9 or adjusted to 10.0 mL with the solvent last used.

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

7.11 If further concentration is indicated in Table 1, add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.12 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a Teflon-sealed screw-cap vial and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

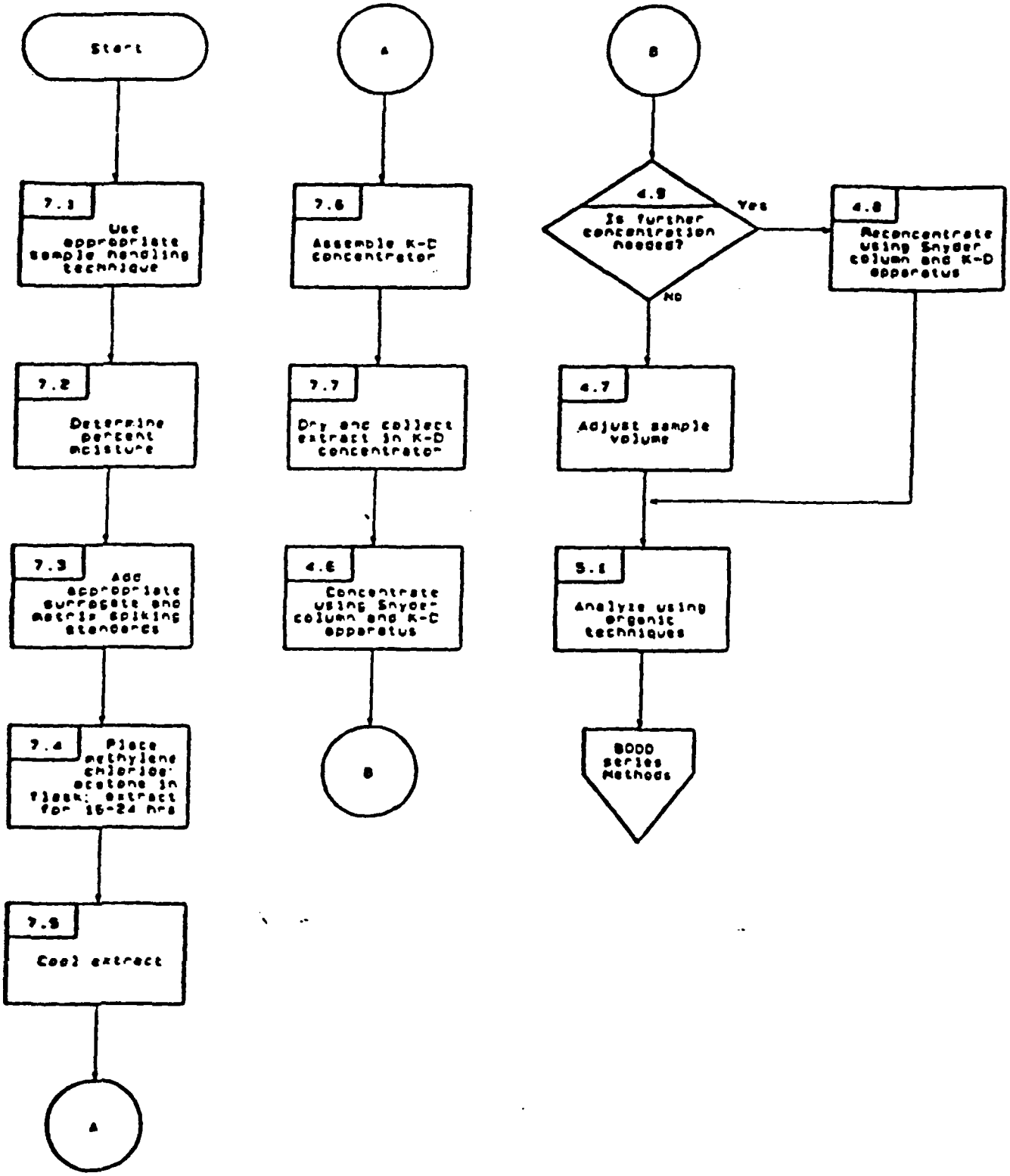
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3540C

SOXHLET EXTRACTION



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