Method AK 102

For Determination of Diesel Range Organics
Version 04/08/02

1. Scope and Application

1.1 Objectives

1.1.1 This method is designed to measure the concentration of Diesel Range Organics (DRO) in water and soil. This corresponds to an n-alkane range from the beginning of C_{10} to the beginning of C_{25}, and a boiling point range of approximately 170° C to 400°C. (See Figure 1 of this method)

1.1.2 Components with boiling points greater than the start of C_{25} present in products such as motor oils or lubricating oils are detectable under the conditions of the method.

1.2 Quantitation Limits

Practical quantitation limits (PQL) for this method for analysis of DRO must not exceed 20 mg/kg for soils and 800 μg/L for waters.

1.3 Dynamic Range

Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. Linear range is dependent in part upon column type, detector sensitivity, and injection volume. Typically, the approximate range is 1 mg/L to 100 mg/L as diesel.

1.4 Experience

This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of solvent extractions and gas chromatographs as quantitative tools.

2. Method Summary

2.1 This method provides gas chromatographic conditions for the detection of semi-volatile petroleum products such as diesels. Other non-petroleum compounds with similar characteristics and boiling points, may also be detected with this method. One liter of water or 25 grams of soil is the recommended sample size. Samples must be spiked with a surrogate compound and extracted with methylene chloride. The extract is dried and concentrated. An aliquot of the extract must be injected into a capillary column gas chromatograph equipped with a flame ionization detector (FID), which has been temperature programmed to facilitate separation of organic compounds. Quantitation must be performed by comparing the total chromatographic area between and including the peak start of C_{10} to the peak start of C_{25}, including both resolved and unresolved

components, based on FID response compared to a diesel calibration standard (see Section 3.2 of this method). Integration must be performed using forced baseline-baseline integration.

2.2 This version of the method was developed by Mary Jane Pilgrim, Ph.D. and is based, in part, on a modification of the American Petroleum Institute consensus "Method for the Determination of Diesel Range Organics," Revision 2, 2/5/92 [11], supplemented with information gathered by the State of Alaska, Department of Environmental Conservation, State Chemistry Laboratory, with support from the Storage Tank Program. It is based in part on EPA Methods 8000 and 8 100, SW- 846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* [1], adopted by reference in 18 AAC 78.090(i), Method OA-2 [2] and work by the EPA Total Petroleum Hydrocarbons Method Committee [3], and the State of Oregon, "Total Petroleum Hydrocarbon Methods" QAR 340-122-350 dated December 11, 1990.

3. Definitions

3.1 Diesel Range Organics (DRO**):** All chromatographic peaks, both resolved and unresolved, eluting between the peak start of n-decane (C_{10}) and the peak start of n-pentacosane (C_{25}) Quantitation is based on direct comparison of the area within this range to the total area over the same (C_{10} - C_{25}) range of the calibration standard as determined by FID response using forced baseline-baseline integration. Surrogate peak areas shall be determined by valley to valley integration.

3.2 Diesel Calibration Standard (DCS): Commercial #2 diesel fuel or equivalent hydrocarbon mixture in which greater than 95% of the hydrocarbon mass elutes within the diesel change diluted to appropriate concentrations in methylene chloride. The DCS serves as a calibration standard for DRO.

3.3 Surrogate: Ortho-terphenyl or equivalent. The surrogate must be spiked into all extracted samples and standards prior to extraction.

3.4 Calibration Verification Standard (CVS): A quality control standard, prepared as in Section 3.2 of this method, but with a diesel range hydrocarbon mixture from a source other than that used to prepare the Diesel Calibration Standard. It is used by the laboratory to verify the accuracy of calibration. Greater than 95 % of the hydrocarbon mass must elute between the diesel range.

3.5 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial #2 diesel fuel the same as that used to make the Diesel Calibration Standard (see Section 3.2 of this method). The spike recovery is used to evaluate method control (see Table 1 of this method).

3.6 Retention Time Window Standard: A mixture of the normal alkanes n-decane and n-pentacosane (C_{10} and C_{25}) which is analyzed once every 24 hour "day" or with each batch

of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard serves to define the retention time window for DRO.

3.7 Internal Standard: Alpha androstane, used to normalize DRO concentrations. Use of an internal standard is recommended, but not required.

3.8 Standard Soil: Ottawa sand, Norwood loam, Houston black clay, or other standard soil with characteristics which match the field samples as closely as possible, used in quality control samples.

3.9 Continuing Calibration Standard (CCS): A mid-range working standard diluted from the Diesel Calibration Standard, used to verify that the analytical system is operating in a manner comparable to that at the time of initial calibration.

3.10 Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit.) Each laboratory must demonstrate and periodically update method detection limits for each analyte of interest.

3.11 Practical Quantification Limit (PQL): is defined as 5 times the MDL.

3.12 Method Blank – also known as a procedural blank demonstrates that the apparatus and reagents used to perform the method are free from contamination.

3.13 Instrument Blank – demonstrates that the instrument is free from contamination.

3.14 Solvent Blank – demonstrates that the solvent (in this case methylene chloride) used in the method is free from contamination. It should not go through the procedure. It may also serve as an instrument blank.

3.15 Other terms are as defined in SW-846 [1].

4. Interferences

4.1 Other organic compounds including, but not limited to, animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, phthalate esters and biogenic terpenes are measurable under the conditions of this method. Heavier petroleum products such as lubricating oil and crude oils also produce a response within the retention time range for DRO. As defined in the method, the DRO results include these compounds.

4.2 Method interferences may be reduced by washing all glassware with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Heating the glassware to reduce contaminants should not be necessary if this cleaning method is followed. At least

one blank must be analyzed with each extraction batch to demonstrate that the laboratory samples are free from method interferences.

4.3 High purity reagents must be used to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of a solvent blank to check for instrument contamination.

5. Safety Issues

5.1 The toxicity or carcinogenicity of each reagent in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. 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 chemical analysis. Additional references to laboratory safety should be available and identified for use by the analyst.

5.2 A hearing protection device should be used when performing sonication.

6. Apparatus and Materials

(Unless otherwise indicated, all apparatus and materials are suggested only.)

6.1 Glassware

6.1.1 4-oz. amber glass wide mouth jars with Teflon-lined screw caps.

6.1.2 Separatory funnel – 2000-mL with Teflon stopcock.

6.1.3 Continuous liquid-liquid extractor - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, New Jersey, P/N6841-10, or equivalent).

6.1.4 Concentrator tube. Kuderna-Danish 10-mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.1.5 Evaporative flask, Kuderna-Danish 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.1.6 Snyder column, Kuderna-Danish three ball macro (Kontes K-503000-0121 or

equivalent). Rotary evaporation set-up may be used alternatively.

6.1.7 Jars: One liter amber glass, with Teflon lined screw caps.

6.1.8 Two mL glass vials with Teflon-lined cap (autosampler vials).

6.1.9 Disposable pipettes: Pasteur.

6.1.10 Graduated cylinders: 250-mL.

6.1.11 Glass or Teflon funnels.

6.2 Boiling chips –Boiling chips must be decontaminated in a manner appropriate for the material.

6.3 Micro syringes 1-µL, 5-µL, 10-µL, 25-µL, and 100-µL.

6.4 An analytical balance capable of accurately weighting 0.0001 g should be used for preparing standards and percent moisture determination. A top-loading balance capable of weighing to the nearest 0.01 g should be used for sample preparation and percent moisture determination.

6.5 Stainless steel spatula.

6.6 Gas Chromatography

6.6.1Gas Chromatography: Analytical system including appropriate gas supply and all required accessories, including a Flame Ionization Detector (FID), column supplies, gases, and syringes. A data system capable of determining peak areas using a forced baseline – baseline projection is required. A data system capable of storing and reintegrating chromatographic data is recommended.

6.6.2 Columns

6.6.2.1 Column 1:HP5MS 30 M x 0.32 mm 0.25 micron film thickness or equivalent.

6.6.2.2 Other Columns may be used - capillary columns may be essential to achieve the necessary resolution. The column must resolve C_{10} from the solvent front in a midrange DCS or CVS must resolve C_{24} from C_{25}.

6.7 Sonication.

6.7.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems-Ultrasonics, Inc., Model W-385 (475 watt)

sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2inch Tapped Disrupter Horn) plus No. 2073/4inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

6.7.2 A Sonabox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).

6.8 Soxhlet extraction apparatus as described in SW-846, Method 3540 [1].

6.9 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

7. Reagents and Standards

7.1 Reagent Water: Water that has been shown to be free from target analytes and interfering substances.

7.2 Methylene Chloride - pesticide grade or equivalent. At a minimum, the solvents must be shown to be free from DRO.

7.3 Sodium Sulfate - (ACS grade) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray or by extracting three times with methylene chloride and drying at 100 ±5° C. Incomplete cleaning of sodium sulfate can result in DRO contamination of samples.

7.4 Stock Standard Solutions - Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in Section 7.2 above. Standard preparation should follow guidelines in SW-846 [1]. All standards prepared by the laboratory must be stored without headspace at -10 to -20°C and protected from light. Marking of the meniscus is helpful in maintaining stock standard integrity. Standards must be replaced within 6 months of preparation. Standards should be checked regularly to assure their integrity. Standards, which are purchased pre-made from commercial suppliers, may be kept for the life, and under the conditions, specified by the manufacturer if different than described in this paragraph.

7.4.1 Optional Stock Internal Standard: 1000 µg/mL 5 alpha-androstane. Other internal standards may be used provided they do not interfere with the DRO components.

7.4.2 Recommended Surrogate Control Standard: 200 µg/mL ortho-terphenyl (OTP). A working solution is made at 20 µg/mL (recommended concentration) in methylene chloride.

7.4.3 Diesel Calibration Standard: Diesel #2 is used to prepare stock calibration standards in methylene chloride. No fewer than 3 concentrations of this DCS are

used for instrument calibration. A five-point calibration curve is recommended. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in project samples should define the working range of the GC. A mid-range dilution of this blend serves as the Continuing Calibration Standard.

7.4.4 Retention Time Window Standard: A stock solution of C_{10} and C_{25} each at a level of at least 2000 µg/mL. This blend of alkanes serves as a retention time window defining mix for DRO.

7.4.5 Stock Calibration Verification Standard (CVS): Provide a stock source of commercial diesel #2 other than that used to prepare the DCS, as described in Section 7.4.3 of this method. A working solution is made at a recommended concentration of 5000 µg/mL in methylene chloride.

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

8.1 Water samples are collected in one liter amber glass containers with Teflon lined screw caps and acidified to pH 2 or less with HCl.

8.2 Soils are collected in a core tube, or 4 or 8 oz amber glass jar with Teflon-lined lid. The samples are stored at 4° ±2° C from the time of collection until extraction. Extraction must be performed on waters and soils within 14 days [1]. All analyses of extracts must take place within 40 days.

8.3 Soil samples to be analyzed for both volatiles and DRO may be collected in the same, methanol preserved container and stored as for GRO (AK101). If this option is selected, the mechanics of the collection, preservation, and container should be discussed with the client before sampling kit preparation. DRO extraction and analysis must still meet the requirements of Section 8.2, above.

8.4 Performance Evaluation (PE) Samples must be obtained from a supplier approved by The NELAC Institute (TNI) or a supplier approved to ISO 17043 standards.

9. Procedure

9.1 Sample Preparation

The preferred method for water extraction is SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction), and for soil samples Method 3540 (Soxhlet Extraction). However, any sample extraction technique which meets the quality assurance requirements specified in Section 10 and Table 1 of this method may be used, and the extraction solvent is methylene chloride.

9.1.1 Water extraction - Separatory Funnel.

9.1.1.1 Measure a 1-L portion of the sample and transfer to a 2-L separatory funnel. If the sample is in a 1-L or smaller bottle, mark the water meniscus on the side of the sample bottle. Measure the exact volume by adding tap water to the bottle to the marked level, and then transferring the volume of tap water to a 1-L graduated cylinder. Use no more than 1-L of sample per 2-L separatory funnel. For blanks and quality control standards, pour 1-L of reagent water (see Section 7.1 of this method) into the separatory funnel.

9.1.1.2 Check and note the pH of the sample. If the field samples have been preserved with HCl, it is recommended that the quality control samples and blanks be preserved in the same way.

9.1.1.3 Add 1 mL of surrogate standard (Section 7.4.2 of this method, recommended level of 20 µg/mL if o-terphenyl is used).

9.1.1.4 For every batch or 20 samples extracted (whichever is more frequent), prepare duplicate LFBs. Daily or for every 20 samples (whichever is more frequent), prepare a method blank using 1-L of reagent water. Surrogate must be added to both the LFBs and the method blank.

9.1.1.5 For samples, add 60 mL methylene chloride to the sample bottle to rinse the inner walls after the sample has been transferred to the separatory funnel. **Do not** cap and shake the bottle, rinse the glass only; then transfer the solvent to the separatory funnel. Extract the sample by shaking it for no less than two minutes with frequent ventilation.

9.1.1.6 Allow the layers to separate (approximately 10 minutes rest after shaking).

9.1.1.7 Drain the bottom layer (methylene chloride).

9.1.1.8 Repeat the extraction twice more, using a 60 mL aliquot of methylene

chloride each time. Collect the solvent in the same vessel as described in Section 9.1.1.7 of this method.

9.1.1.9 Concentrate extracts to 1 mL at a temperature not to exceed 55° C or that recommended by the manufacturer of concentration apparatus being used. Transfer extracts to GC vials for analysis. Extracts should be stored in a freezer at <10° C. Record the information for the extraction and concentration steps.

Note: The concentration step is critical; losses of target compounds can occur if care is not taken.

9.1.1.10 If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5-10 mL). Transfer to a labeled vial of appropriate size with Teflon-lined cap, mark the meniscus. Extracts should be stored in a non-frost free freezer at <-10° C.

9.1.1.11 Record information for the extraction and concentration steps.

Note: The extraction and concentration steps must be performed under a hood. Methylene chloride a potential health hazard (see MSDS).

9.1.2 Soil Preparation - Soxhlet Extraction

9.1.2.1 Decant any water layer that may accompany the solid layer in the sample. Note what percent of the sample the water represents and, if sufficient volume exists, extract and analyze the water for DRO. Also note the apparent condition of the sample (presence of foreign materials, variable particle size, presence of oil sheen, multiple phases, etc.).

9.1.2.2 Weigh 10 g to 30 g of the original sample into an extraction thimble. Add an equal weight of anhydrous sodium sulfate and stir the mixture well with a stainless steel or Teflon® spatula. The sample should have a grainy texture - if the sample clumps, add more sodium sulfate until a grainy texture is achieved and note the addition. (Do this for all samples and standards.)

9.1.2.3 Place loaded thimbles in extractors and add surrogate to both field and quality control samples.

9.1.2.4 Add spiking solution to the duplicate LFBs. These quality control samples should contain 10 g of methylene chloride rinsed Ottawa Sand or alternative standard soil. In addition, prepare a method blank.

9.1.2.5 Add 300 mL of methylene chloride to the 500-mL extraction flask. Less extraction solvent may be used if the quality control criteria specified in Section 10 and Table 1 are met. Also add a few methylene chloride washed, boiling chips to the flask. Connect the extractor to the flask and the condenser to the extractor. Allow samples to extract for 18-24 hours, or as long as necessary to achieve optimum surrogate recovery. Be sure that coolant is flowing around the condensers.

9.1.2.6 Recommendation: After extraction, dry the extract with anyhydrous sodium sulfate. (This assures that the extract is water-free before concentration.)

9.1.2.7 Transfer extract into a clean concentration vessel and concentrate extracts to 1 mL at a temperature not to exceed 55° C or that recommended by the manufacturer of concentration apparatus being used. Transfer extracts to GC vials for analysis. Extracts should be stored in a freezer at <10° C. Record the information for the extraction and concentration steps.

9.1.3 Moisture Determination for Solids

9.1.3.1 Moisture determinations must accompany all soils data (reported in mg/dry kg) so the client can, at will, determine the results in the original soil condition. Because of the potential for high petroleum compound concentrations in the soil, all drying should be done under a functioning hood.

9.1.3.2 To determine percentage of moisture, pre-weigh an aluminum weighing boat. Weigh 5 -10 g of the sample into the boat and record both weights to the nearest 0.01 g. Dry the sample overnight in a warm (105°C) oven.

9.1.3.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.01 g. Record the weight.

9.1.4 Dilution Technique

9.1.4.1 This is used for product or waste samples for which extraction is not appropriate and which are soluble in methylene chloride.

9.1.4.2 Weigh 1 g of sample into a 10-mL volumetric flask. Dilute to 10-mL with methylene chloride. Transfer to a 12 mL vial with a Teflon lined lid. Mark meniscus and store at <4°C. (Refer to EPA SW-846 Method 8270C for storage temperature.)

9.2 Gas Chromatography

9.2.1 Conditions (Recommended):
Set helium column pressure to 20#. Set column temperature to 40° C for 2 minutes, then ramp at a rate of 12° C/min to 320° C and hold for 15 min. (run time = 36 minutes). Set FID Detector to 320° C and injector to 280° C.

9.2.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

9.2.2.1 Resolution of the methylene chloride solvent front from C_{10}.

9.2.2.2 The separation number, TZ, should be greater than 15 for C_{24} and $C_{25,}$ if RRO is to be analyzed concomitantly.

$$TZ = [(\text{retention time } C_{25} - \text{retention time } C_{24})/ (W \tfrac{1}{2} \text{ of } C25 + W \tfrac{1}{2} \text{ of } C24)] -1$$

Where "W½" = peak width at half-height

9.2.2.3 The column must be capable of separating typical diesel components from the surrogate and internal standards. In particular, there are potential problems with the resolution of n-C_{19} from ortho-terphenyl and n-C_{21} from 5 alpha-androstane at varying relative concentrations.

9.3 Calibration

9.3.1 Calibrate the GC, set up as in Section 9.2 of this method. A minimum of three concentrations of DCS (five concentrations are recommended).

9.3.2 Choose DCS concentrations to cover the DRO range expected in the samples, or the linear range of the instrument, whichever is less. Linearity of the calibration curve at the PQL must be determined.

9.3.3 Curve fit must be linear regression with a R^2 of 0.995 or better, quadratic fit with a R^2 of 0.995 or better, or if using response factors, the average percent relative standard deviation (%RSD) is less than 25% over the working range.

9.3.4 The calibration curve must be confirmed using the CVS (see Section 7.4.5 of this method). This standard verifies the accuracy of the calibration. The concentration of the CVS should be within the expected concentration range of the samples to be analyzed. The working RF or calibration curve must be verified on each working day (24 hours) by the injection of a CCS (see Section 7.4.3 of this method) at a concentration mid-point on the calibration curve. The CCS is a diluted aliquot of the same standard used to initially calibrate the instrument. If the response for the CCS

varies from the predicted response by more than 25%, a new calibration curve must be prepared.

9.4 Retention Time Window Definition:

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (see Section 6.6 of this method). Make three injections of the Retention Time Window Standard (see Section 7.4.4 of this method) and surrogate throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

9.4.2 Calculate the standard deviation of the three absolute retention times for decane and pentacosane and the surrogate.

9.4.2.1 The retention time (RT) window for individual peaks is defined as the average RT plus or minus three times the standard deviation of the absolute retention times for each component.

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use ±0.05 min. in place of the standard.

9.4.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or instrument conditions changed. The data must be retained by the laboratory for at least a year.

9.4.4 Retention time windows must be verified regularly and updated no less frequently than once a year.

9.5 Gas Chromatograph Analysis

9.5.1 Samples are analyzed by GC/FID. Optimum injection volumes (2 μL using the conditions established in Section 9.2 of this method) must be established for specific instrument conditions.

9.5.2 For internal standard calibration, the internal standard is spiked into each sample and standard at a concentration of 200 μg/mL of sample extract. Twenty μL of 5-alpha androstane stock at 1000 μg/mL may be spiked into the 1 mL final volume or a corresponding amount may be added to an aliquot of the final extract. (Note: **DRO values >2000 μg/mL may lead to measurement bias due to coelution with the internal standard.)** Internal standard calibration should not be used when DRO exceeds 5,000 μg/mL in the final extract.

9.5.3 If initial calibration (see Section 9.3 of this method) has been performed, verify the calibration by analysis of a mid-point CCS. With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window

Standard (Section 7.4.4 of this method).

9.5.4 Calculate the percent difference of the response factor from the mean response factor as in Section 9.3.2 of this method. This is done for DRO as a group from the CCS. If the response factor has a percent difference greater than 25%, corrective action must be taken.

9.5.5 A solvent blank (methylene chloride) may be analyzed each day to determine the area generated from normal baseline noise under the conditions prevailing in the 24 hour period. This area is generated by projecting a horizontal baseline between the retention times observed for the peak start of C_{10} and the peak start of C_{25}. This blank is integrated over the DRO area in the same manner as for the field samples and is reported as the solvent blank. (Refer to Section 4 of this method) **Do not baseline subtract. This information is for data interpretation purposes only.**

9.5.6 Blanks should also be run after samples suspected of being highly concentrated to prevent carryover. If the blank analysis shows contamination above the practical quantitation limit, the column must be baked out and subsequent blanks analyzed until the system is shown to retain contaminant at concentrations less than the PQL.

9.5.7 If the DRO concentration exceeds the linear range of the method (as defined by the range of the calibration curve) in the final extract, corrective action must be taken. The sample should be diluted or external standard calibration should be used. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve

9.6 Calculations:

9.6.1 Percent Moisture Calculation for Soils

$$\% \text{ Moisture} = [(A-C)/(A-B)] \times 100$$

Where: A = weight of boat + wet sample
B = weight of boat
C = weight of boat + dry sample

Note: Make sure drying oven is placed under a hood. Heavily contaminated soils will produce strong organic vapors.

9.6.2 Internal Standard Calibration: The concentration of DRO in the sample must be determined by calculating the absolute weight of analyte chromatographed from a summation of peak response for all chromatographic peaks eluting between the peak start of n-decane and the peak start of n-pentacosane, using the calibration curve or the response factor determined in Section 9.3 and Section 9.4 of this

method (Retention Time Window Definition). The concentration of DRO is calculated as follows:

Aqueous/Soil samples:

$$Cs = \frac{(Ax)(Cis)(D)(Vt)}{(Ais)(RF)(Vs)}$$

Where: Cs = Concentration of DRO (mg/L or mg/kg).
Ax = Response for the DRO in the sample, units in area.
RF = Response Factor from CCS (see Section 9.3.3).
Ais = Response for the internal standard, units same as for Ax.
Cis = Internal standard concentration (mg/mL).
Vt = Volume of final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.3 To calculate mg/dry kg for soil samples,

$$\text{mg/dry kg DRO} = \frac{Cs}{1-(\%\ \text{moisture}/\ 100)}$$

The % moisture calculation must be included in the data package (see Section 9.6. 1). Some software programs are capable of performing these calculations with minimal analyst intervention.

9.6.4 External Standard Calibration:

Aqueous/Soil samples:

$$Cs = \frac{(Ax)\ (A)\ (Vt)\ (D)}{(As)\ (Vs)}$$

Where: **Cs** = Concentration of DRO (mg/L or mg/kg).
Ax = Response for the DRO in the sample, units in area.
As = Response for the external standard, units same as for Ax.
A = External standard concentration (mg/mL).
Vt = Volume of Final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, then D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.5 Some software programs are capable of performing Sections 9.6.1 and 9.6.3 of this method, with minimal analyst intervention. Additionally, some software programs can "update" a calibration curve based on the response of the CCS. If a calibration curve is

updated in this manner, a valid CVS must be analyzed and results must fall within the Quality Control Criteria specified in Section 10 and Table 1 of this method before field samples can be analyzed.

10. Quality Control

10.1 Curve Verification Standard (CVS)

10.1.1 The CVS is not extracted.
10.1.2 The CVS is analyzed once with calibration standards to verify calibration curve.
10.1.3 The CVS recovery requirement is 75-125% of true value.

10.2 Continuing Calibration Samples (CCS)

10.2.1 The CCS is not extracted.
10.2.2 The CCS is analyzed at the start and end of an analytical batch and for every 20 samples in that batch.
10.2.3 The CCS recovery requirement is 75-125% of true value.

10.3 Blanks

10.3.1 Instrument Blank may be analyzed with each analytical batch to demonstrate that the system is free from contamination.
10.3.2 Method Blank must be analyzed with each extraction batch.
10.3.3 BLANK SUBTRACTION IS NOT ALLOWED. Blanks are reported by value. This information is for data quality assessment purposes only.
10.3.4 Other blanks may be analyzed as necessary following the recommendations of Chapter 2 Section 9 of the *UST Procedures Manual*.

10.4 Lab Fortified Blanks (LFB)

10.4.1 LFB is extracted using the method procedure.
10.4.2 One LFB is analyzed with each analytical batch
10.4.3 The LFB recovery requirement is 75-125% of true value.
10.4.4 If any LFB recovery fails to meet method criteria, appropriate corrective action must be taken. See 10.7, “Corrective Actions”.

10.5 Matrix Spike (MS) and Matrix Spike Duplicates (MSD)

10.5.1 MS & MSD are samples that are spiked with DCS to produce a known concentration greater than the sample background concentration. Both are processed as samples.
10.5.2 MS & MSD are analyzed only when requested.
10.5.3 There are no RPD or recovery requirements for MS and MSD.

10.6 Surrogate

10.210.6.1 The surrogate should be spiked at a level to produce a recommended extract

concentration of 20 μg/mL.

10.6.2 Surrogate recoveries must be 60-120% for laboratory control samples (CCS, CVS, method blank, LFB) and 50-150 % for field samples(all other samples).

10.6.3 If any surrogate recovery fails to meet method criteria, corrective action must be taken. See 10.7, "Corrective Actions".

10.6.4 If field samples show poor surrogate recovery which is not attributable to laboratory error, DRO results must be flagged. Re-sampling, matrix spikes or other remedial action is at the discretion of the client and is not the responsibility of the laboratory.

10.7 Corrective Action

10.7.1 The actions listed below are recommended and may not apply to a particular failure.

10.7.2 Check for matrix interference or carry-over.

10.7.3 Check for errors in calculation and that concentrations of surrogates and internal standards are correct.

10.7.4 Check that instrument performance meets method criteria.

10.7.5 Re-process the data.

10.7.6 Re-analyze the extracts.

10.7.7 Extract additional aliquots of the failing sample(s) and re-analyze.

10.7.8 Collect replacement samples

11. Method Performance

11.1 Single lab method performance data for the DROs method in Ottawa sand and other soil types is presented below.

11.2 Results for diesel spikes (methylene chloride extraction direct injection, soils) using a blend of different diesel products.

		Diesel Spike Amount	
23	**Matrix**	**mg/kg**	**Percent**
24			**Recovery**
	Ottawa Sand	70	97
	Ottawa Sand	70	98
	Glacial Blue Clay	70	70
	Glacial Blue Clay	70	76
	Forest Loam	70	136
	Forest Loam	70	163
	River Sediment	70	142
	River Sediment	70	167
	Marine Sand	70	95
	Marine Sand	70	88

Notes: Analyses performed by State of Alaska, DEC Laboratory. Diesel used =A mixture made of a blend of equal weights (1:1:1) of arctic diesel, diesel #1, and diesel #2, mixed together to form a composite diesel fuel. All highly organic soil matrices showed high analyte recovery due to naturally occurring DROs.

11.3 The method detection limit for soil calculated according to 40 C.F.R..136, Appendix B (1994) was 1.6 mg/kg (external standard calibration, Ottawa sand) at SCL.

12. References

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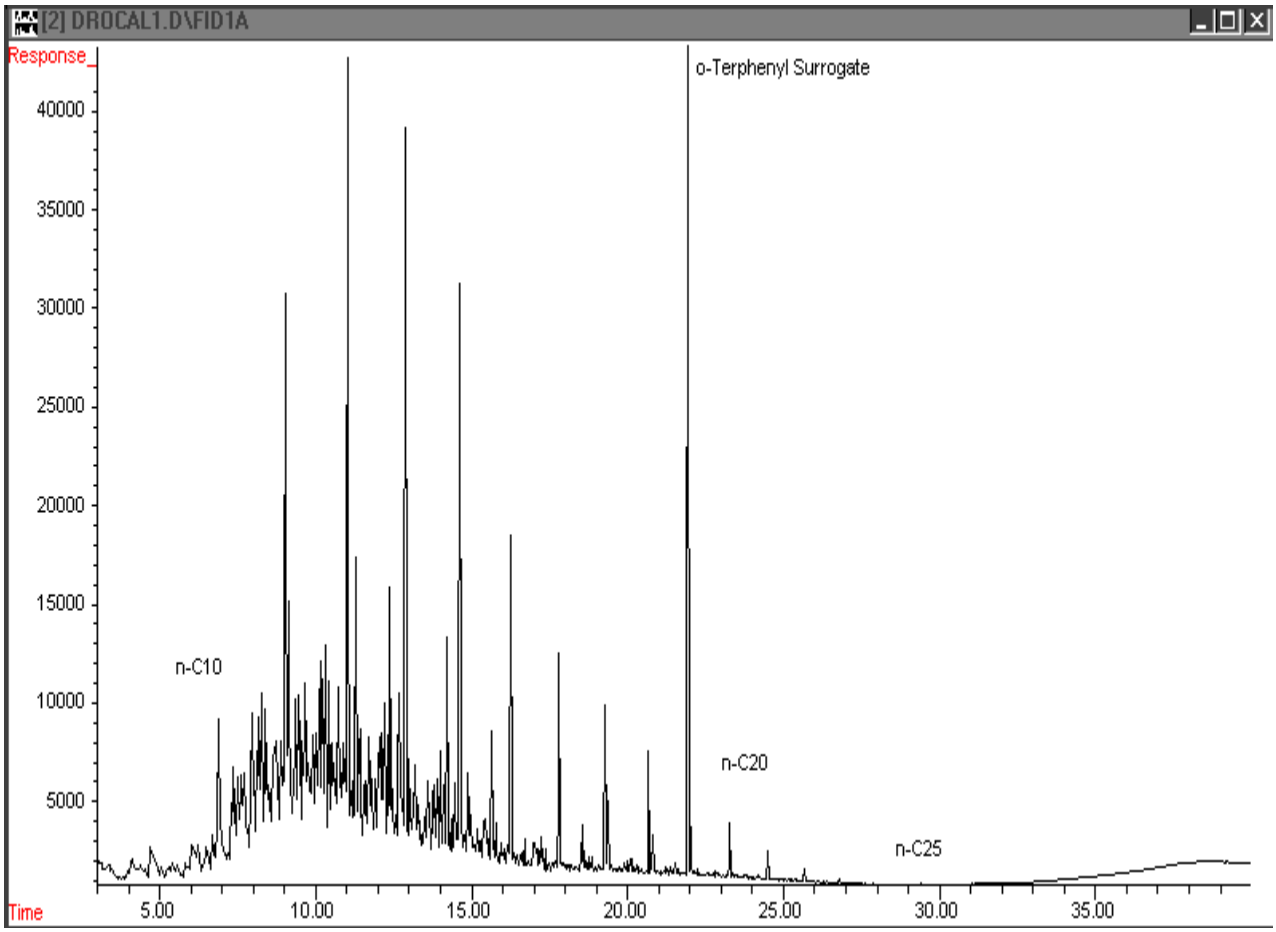
Figure 1. Diesel Range Organics, Fuel Oil #2



Method AK102, Table 1
Acceptance Criteria for Quality Control

	Analyze Spike Concentration		Control Limits	
	Water (mg/L)	Soils (mg/Kg)	% Recovery	Relative% Difference
Lab Fortified Blanks	0.5-2.0		75-125	20
Continuing Calibration			75-125	
Calibration Verification			75-125	
Surrogate Recovery:				
Laboratory Control Sample**:	0.02	0.8	60-120	
Field Sample:	0.02	0.8	50-150	

- Suggested concentrations. May vary with matrix.
- **Laboratory Control Sample is any laboratory prepared sample used for quality control except calibration standards.

Field criteria from voluntary contribution of method performance information from Approved laboratories, and method performance at SCL.