OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

METHODS 8000/8100 (MODIFIED)

DIESEL RANGE ORGANICS (DRO)

1. SCOPE AND APPLICATION:

1.1. This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a hydrocarbon range of C_{10}-C_{28} and a boiling range between approximately 170^{o}C and 430^{o}C.

1.2. The Practical Quantitation Limit (PQL) of this method for total diesel range organics is approximately 0.1 mg/l for waters and 10 mg/kg for soils, whereas the PQL for individual components is 0.05 mg/l for waters and 5 mg/kg for soils..

1.3. This method is based on a solvent extraction gas chromatography procedure. This method should be used by, or under the supervision of, analysts experienced in solvent extraction and the use of gas chromatographic data. The analysts should be skilled in the interpretation of gas chromatographs and their use as a quantitative tool.

1.4. This method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of this method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional analyses may be performed. Such additional analyses are not within the purview of this method.

2. SUMMARY OF METHOD:

2.1. This method provides the gas chromatographic conditions for the detection of volatile petroleum fractions such as diesel, fuel oil #2, or kerosene. Samples are analyzed using extraction to dissolve the organic components. The extract is dried, concentrated, and injected into a gas chromatograph. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection and quantitation are based on flame ionization detector (FID) response to a diesel component standard.

2.2. This method is suitable for the analysis of waters, soil, and wastes.

2.4. This method is based in part on: 1) USEPA SW-846: Methods 8000, and 8100; 2) work by the EPA Total Petroleum Hydrocarbons Methods Committee; and 3) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

3. DEFINITIONS:

3.1. Diesel Range Organics (DRO): All chromatographic peaks eluting between n-decane (n-C_{10}) and n-octacosane (n-C_{28}). Quantitation is based on a direct comparison of the total area within this range to the total area of the ten components of the Diesel Component Standard.

3.2. Diesel Component Standard: A ten component blend of typical diesel compounds(see Table 1). This standard serves as the quantitation standard and a retention time window for diesel range organics..

3.3. Diesel Component Spike: A duplicate reagent water or method blank sample spiked with the Diesel Component Standard and analyzed along with samples as a quality control check.

3.4. Trip Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials, and carried along with samples to ensure that any contamination found in the samples is in fact in those samples.

3.5. Other terms as defined in SW-846.

4. INTERFERENCES:

4.1. Other organic compounds, such as chlorinated solvents, phenols, and phthalate esters are measurable. As defined in this method, the DRO results include these compounds. Neat products should be quantified by specific analysis for the product in question. (The term "neat product" is defined as a product containing only a single compound.) An example of this is a spill or a storage tank of benzene.

4.2. Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and/or storage. Trip blanks should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.3. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with deionized water, hexane, and methylene chloride. Glassware is then kept in a drying oven at 105^{o}C to ensure a contaminant-free apparatus for

subsequent sample analysis. Reagent blanks must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interferences.

4.4. Contamination can occur by carryover whenever high-level and low-level samples are analyzed sequentially. . A method blank of organic-free water is run through this method before processing any samples in order to demonstrate that the system is free of interferences. Additional method blanks must be analyzed after every ten samples, at a minimum, to demonstrate that the system is free of carryover. If, in the professional judgement of the analyst, carryover may have occurred, the sample must be reanalyzed. If a blank exceeds the minimum threshold (PQL) for the analysis, the samples in the preceding set must be reanalyzed.

5. SAFETY ISSUES:

The toxicity or carcinogenity of each reagent used 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 file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in the chemical analysis.

6. APPARATUS:

6.1. Gas Chromatograph: Analytical system complete with a programmable gas chromatograph , a data system to measure peak areas, and all required accessories (detector, column, supplies, etc.).

6.1.1. GC Column: A capillary column such as a 30 m x 0.53 mm I.D., 3.0 µ film DB-5, or any other column capable of resolving typical diesel components. It must resolve n-decane from the solvent peak. Although a suitable packed column may be found, it is recommended that a capillary column be used to attain the required resolution. Typical chromatograms are attached at the end of this document.

6.1.2. Detector: Flame ionization detector (FID).

6.2. Nitrogen evaporator (Zymark TurboVapII or equivalent) and high purity nitrogen gas source. [A Kuderna-Danish (KD) evaporative concentrator may be used as an alternative to this nitrogen evaporator. The KD apparatus consists of a KD flask, Snyder column, and KD receiver tube.]

6.3. Sonicator (Branson Sonifier II or equivalent): Sonicator must be equipped to provide for adjustment of the pulse duration and output.

6.4. Balances: A balance capable of accurately weighing 0.0001 g should be used for the preparation of standards. A top-loading balance capable of weighing to the nearest 0.1 g is suitable for sample weights.

6.5. Sample vials: Wide mouth 60 ml glass vials with teflon/silicone septa for soils and 1-liter amber glass bottles with teflon-lined screw caps for waters.

6.6. Microsyringes: Gas-tight microsyringes in the appropriate sizes in the range of 1 ul to 500 ul syringes.

6.7. Volumetric Flasks: Appropriate sizes with ground-glass stoppers.

6.8. Disposable pipets: Pasteur-type, 5.75 in, or equivalent.

6.9. Spatula/scoop: Stainless steel

6.10. Sampling devices: ENCORE type or equivalent.

7. REAGENTS:

7.1. Reagent water: Organic-free water.

7.2. Solvent: Methylene chloride, pesticide grade or equivalent.

7.3. Sodium Sulfate: ACS grade, granular, anhydrous. Purify by heating at 400^{o}C for 4 hours and allowing to cool in a drying oven. Store in a drying oven until ready for use.

7.4. Sodium Chloride: ACS grade, crystals.

7.5. Standard Solutions: Preparation of stock standard solutions should be performed using appropriate volumetric glassware. Solutions should be stored in Teflon-sealed screw-cap bottles, with minimal headspace, at -10^{o}C to -20^{o}C, protected from light.

7.5.1. Stock DRO Standard : An acceptable stock standard for DRO components is the commercially-available standard as described in Table 1. The following procedure is provided as an alternative to commercially-available and certified solutions.

Standards should be replaced after six months, or sooner if comparison with check standards indicates a problem.

7.5.1.1. Place about 8 ml of a solvent listed in 7.2 above in a 10 ml tared, ground-glass stoppered volumetric flask. Allow the flask to stand unstoppered for about 10 minutes, or until all solvent-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.5.1.2. Using a 100 ul syringe, immediately add 20 ul to30 ul of the diesel component standard to the flask. [The liquid must fall directly into the solvent without contacting the neck of the flask.] Reweigh the flask.

7.5.1.3. Dilute to volume, stopper, and mix by inverting the flask three times. Calculate the concentration in ug/ml from the net gain in weight. (When compound purity is assayed at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.)

7.5.1.4. Transfer the stock standard stolution to a Teflon-sealed, screw-cap amber bottle and store at 4^{o}C.

7.5.2. Diesel Component Standard: Using the DRO stock standard, prepare diesel component standard in a solvent listed in 7.2 as needed as a working standard. This standard should be stored with minimal headspace at 4^{o}C and should be checked frequently for signs of degradation or evaporation, especially just prior to preparation of calibration standards.

7.5.3. Calibration Standards: Prepare calibration standards at a minimum of three concentration levels in solvent from the diesel component standard. One of the concentration levels should be at the PQL of the individual components, while the remaining levels should correspond to the working range of the GC.

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING:

8.1. Water samples should be collected without agitation in contaminant-free one-liter amber glass bottles with a Teflon-lined screw cap. The teflon liner must face towards the sample. Cool samples to 4^{o}C immediately after collection. Extraction must be performed within 7 days of collection.

8.2. Soil core samples are collected in wide mouth vials with minimum handling to reduce loss of contaminants. Soil samples may be collected and stored on ice in

ENCORE samplers, or other equivalent sampling devices. These should be collected in sufficient number to provide for backup analysis in the event of breakage. Every effort should be made to minimize handling and avoid excessive disturbance of the soil sample. Cool samples to 4^{o}C immediately after collection.

8.3 Samples must be preserved with 5 ml of 50% HCl at the time of collection. [Sample bottles containing the preservative acid may be supplied by the laboratory in lieu of this field preservation, and should be so noted on the sample collection document.]

8.4. A trip blank must be included with each sample set. If one is not provided, the laboratory must include a note to this effect on the final analytical report for each sample within that set.

8.5. All samples must be analyzed within 40 days of collection, however, water samples must be extracted within 7 days of collection, while soil samples must be placed under solvent within 7 days of collection.

9. ANALYTICAL PROCEDURE:

9.1. Samples are analyzed by GC/FID. Extraction procedures are delineated in 9.4. below. After the extracts are concentrated, a volume is injected directly into the GC. Concentrations noted will be reported in mg/l for water samples and mg/kg for soil samples (on a wet-weight basis).

9.2. Gas Chromatography: Set chromatographic conditions for the recommended column as follows: Initial temperature: 50^{o}C for 4 minutes; then 10^{o}C/min to 300^{o}C; hold for 15 minutes. [Total run time: 40 minutes.] Set FID to 360^{o}C and injector to 350^{o}C. Conditions may be altered as necessary to improve resolution of the diesel range organics. If a column other than the recommended column is used, set the GC conditions to meet the criteria set forth in 6.1.1.

9.3. Retention Time Window and Quantitation:

9.3.1. The retention time window for total DRO is defined as beginning approximately 0.1 min before the retention time of n-decane and ending 0.1 min after the retention time of n-octacosane in the calibration run. Retention time windows for the individual components are similarly established as ± 0.1 min of the retention times in the calibration run.

9.3.2. Quantitation is based on a direct comparison of the area within the range to the total area of the ten components in the diesel component standard,

using a "baseline -to-baseline" integration, as opposed to a "valley-to-valley" integration.

9.3.3. The laboratory must determine retention time windows for the first and last standard on each GC column and whenever a new GC column is installed.

9.3.4. Quantify by summing all peak areas eluting between n-decane and n-octacosane.

9. 4. Sample Preparation:

9.4.1. Water Extraction [Separatory Funnel Method]: This method is based on using a 1-liter separatory funnel. If a larger funnel is used, appropriate adjustment of the sample size may be made, at the discretion of the laboratory.

9.4.1.1. Rinse a one (1) liter separatory funnel with 25 ml of solvent and discard rinse. Rinse a 200 ml Turbo-Vap sample tube with 10 mls of solvent and discard rinse.

Note: The same solvent must be used for calibration standards and extraction.

9.4.1.2. Prepare a drying filter using anhydrous sodium sulfate in a 50 ml reservoir glass chromatography column, or other appropriate glass filtration device. Rinse the prepared filter with 25 ml of solvent and discard rinse.

9.4.1.3. Measure a known volume of sample (800 ml to 900 ml) using a graduated cylinder and transfer the sample to the separatory funnel. Rinse the graduated cylinder with 50 ml of solvent into the separatory funnel containing the sample. Stopper the funnel and shake it vigorously for two (2) minutes, venting the pressure as necessary.

9.4.1.4. Allow the water and organic layers to separate and drain the organic layer into the sample tube through the sodium sulfate drying filter.

9.4.1.5. Perform two additional extractions as above using 50 ml aliquots of solvent and combining the organic layer with that in 9.5.1.4 above.

9 4.1.6. Rinse the drying filter with 25 ml of solvent, draining the rinse into the sample tube.

9.4.1.7. Concentrate the combined extracts and rinse to a volume approximating 1 ml using a Turbo-Vap Concentrator apparatus . Bring the concentrate to a final volume of 5 ml with solvent and store in a new 16mm X 125 mm glass screw-top culture tube sealed with a Teflon-lined cap , or its equivalent.

Note: An alternative concentration technique entails the use of a Kuderna-Danish Evaporative Concentrator apparatus rather than a nitrogen evaporator.

9.4.2. Water Extraction [Continuous Liquid-Liquid Extraction Method]:

9.4.2.1. Place 250 ml of the same solvent used for the calibraton standards in a round-bottom flask. Add a few boiling chips.

9.4.2.2. Add 300 ml of solvent to the extractor flask. When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water into the sidearm by pouring the water down the back of the extractor.

9.4.2.3. Transfer a measured volume of sample (not to exceed 1 liter) into the extractor flask. Record the volume.

9.4.2.4. Add enough reagent water to the extractor flask to allow the solvent in the removable sidearm to just begin to drip into the round -bottom flask. Record the total volume of reagent water that was added to the apparatus.

9.4.2.5. Rinse the ground-glass joint of the condenser wth solvent and place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators. Turn on the heating mantle. Check after 15 minutes to ensure that the solvent is boiling in the round-bottom flask, that solvent is dripping from the lip of the condenser and

that the volume of the solvent in the round-bottom flask is still about 240 ml.

9.4.2.6. Check all extractor joints for leaks. Allow the extraction to proceed for 18 hours to 24 hours. Turn off the heating mantle and allow the apparatus to cool for 30 nimutes to 60 minutes with the water flowing through the condenser.

9.4.2.7. The solvent contained in the round-bottom flask is the extract. Transfer this extract through a sodium sulfate drying filter to to a concentrator tube and concentrate the extract as in 9.4.1.7. above.

9.4.3. Soil/Sediment Extraction: This extraction is based on solvent extraction of the sample. [While sonication is indicated below, extraction may be performed by use of a soxhlet extractor, at the discretion of the laboratory.] The extract is concentrated and an aliquot is injected into the GC.

9.4.3.1. Place a known weight of sample (not to exceed 20 g) in an appropriately-sized glass beaker and add solvent in a 1:1 ratio (mLs of solvent to grams of sample).

9.4.3.2. Add 25 g of dried sodium sulfate to the vial and mix vigorously for 2 minutes. Sonicate the sample/solvent/sulfate mixture for 2 minutes to 5 minutes. Allow sediment to settle and decant solvent layer into a 200 ml sample tube.

9.4.3.3. Add 25 ml of solvent to the sediment and resonicate for an additional 2 - 5 minutes. Decant solvent, combining it with the first extract. Repeat this procedure a third time.

9.4.3.4. Concentrate the combined extracts in accordance with 9.4.1.7 above.

9.4.4. Inject an appropriate volume of the concentrated extract into the GC and proceed with the analysis. If the initial analysis of a sample or a dilution of a sample is found to have a concentration of analytes that exceeds the initial calibration range, that sample must be reanalyzed at a higher dilution. The degree of dilution will be considered adequate when response to all analytes in question are within the calibration range.

9.5. Calculations: The concentration of DRO in the sample is determined from a summation of total peak area for all chromatographic peaks eluting btween n-decane and n-octacosane, using the calibration curve. From linear regression of the GC responses to the calibration standard (R) against their known concentrations (C in mg/l), derive the following linear equation:

$$C = mR + b$$

Using the slope (m) and the intercept (b) from this equation, the concentration of the sample can be calculated from the following equations:

Water Samples:

$$C_S = [(mR_S + b) (V_E) (D)] / V_S$$

Soil Samples:

$$C_S = [(mR_S + b) (V_E) (D)] / W$$

Where: C_S = Concentration of the sample (waters: mg/l; soils: mg/kg on a wet-weight basis);

m = Slope of the calibration curve;

R_S = GC response of the sample within the DRO retention time window;

b = Intercept of the calibration curve;

D = Dilution factor if sample was diluted;

V_E = Total volume of extract in ml;

V_S = Volume of water sample extracted in ml;

W = Wet weight of soil sample in g.

10. CALIBRATION:

10.1. Two multi-level calibrations are required. In each instance, one level at the PQL and a minimum of two other levels represent the working range of the GC. [Total diesel range organics (TDRO) are calibrated separately from the individual components on the flame ionization detector (FID) using the retention time windows discussed in 9 above.]

10.2. Inject the diesel component standard and tabulate the peak area for the ten components against the mass injected. The results are used to prepare a calibration curve by linear regression.

10.3. Each day that samples are run, a calibration standard must be analyzed. If the results of that analysis fall within ± 20% of the expected analysis, the system may be considered to be in control and sample analysis may proceed. If that analysis does not meet these criteria, prepare a new working standard and run a full recalibration before proceeding with the sample analysis.

10.4. The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99. Other criteria may be used to monitor the calibration curve as long as the correlation coefficient is at least 0.99.

11. QUALITY ASSURANCE/QUALITY CONTROL:

11.1. The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with this method by successful analysis of the following:

11.1.1. Analysis of 7 replicates of the diesel component standard at a concentration of 100 ug/l of total DRO in organic-free water with recoveries of all components within ± 40% of the known concentration and precision of all replicates within ± 30%.

11.1.2. Analysis of 7 replicates of DRO_free sand at a concentration of 10 mg/kg of total DRO with all recoveries within ± 40% of the known concentration and precision of all replicates within ± 30%.

11.2. A method blank of organic-free water is analyzed before processing any samples in order to demonstrate the system is free of interferences. Additional method blanks must be analyzed after every ten samples, as a minimum, to demonstrate that the system is free of carryover. If, in the professional judgement of the analyst, carryover may have occurred, the sample must be reanalyzed. If a blank exceeds the minimum threshold (PQL) for the analysis, the samples in the preceding set must be reanalyzed.

11.3. Duplicate diesel component spikes must be run with every batch of 10 or less samples, regardless of whether the samples are waters or soils. The laboratory must analyze these spikes in the same manner as samples. Accuracy and precision of the duplicate water spikes must be within 20% of the known

concentration, whereas that of duplicate soil spikes must be within 40% of the known concentration.

11.4. A reagent solvent blank should be analyzed. If contamination is noted it is the responsibility of the laboratory to determine the source of contamination.

11.5. The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99. Other criteria may be used to monitor the calibration curve as long as the correlation coefficient is at least 0.99.

11.6. If any of the above criteria are not met, the problem must be identified and corrected before further sample analysis may proceed. Any samples run between the last QC samples that meet the criteria and those that fail to do so must be rerun. If this is not possible, the data must be flagged as suspect and so noted in the final report of the analysis.

11.7. The laboratory will maintain appropriate quality control charts of the accuracy and precision of each component of the duplicate spikes in order to identify possible trends before the system goes out of the acceptable limits on accuracy and precision.

12. METHOD PERFORMANCE:

The recommended practical quantitation limits (PQL) are as listed in Table 2.

TABLE 1

DIESEL COMPONENT STANDARD

Commercially available from Supelco Inc as the UST Modified Diesel Range Organics, Supelco Part # 4-8166, in a concentration of 1000 ug/ml of each component in hexane:

n-Decane	n-Eicosane
n-Dodecane	n-Docosane

n-Tetradecane	n-Tetracosane
n-Hexadecane	n-Hexacosane
n-Octadecane	n-Octacosane

TABLE 2

RECOMMENDED PRACTICAL QUANTITATION LIMITS

PARAMETER	WATER (mg/l)	SOIL (mg/kg)
Total Diesel Range Organics	0.100	10.0
n-Decane	0.050	5.0
n-Dodecane	0.050	5.0
n-Tetradecane	0.050	5.0
n-Hexadecane	0.050	5.0
n-Octadecane	0.050	5.0
n-Eicosane	0.050	5.0
n-Docosane	0.050	5.0
n-Tetracosane	0.050	5.0
n-Hexacosane	0.050	5.0
n-Octacosane	0.050	5.0