Modified

D R O

Method for Determining Diesel Range Organics

WISCONSIN DNR

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MODIFIED METHOD FOR DETERMINATION OF DIESEL RANGE ORGANICS

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 point range between approximately 170°C and 430°C. As defined in the method, other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils are measurable. DRO results include these compounds/products.

1.2 The Limit of Quantitation (LOQ) of this method for diesel range organics is 10 mg/kg or less for soils and 0.1 mg/L or less for groundwater.

1.3 This method is based on a solvent extraction, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in solvent extraction and the use of gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use.

1.4 The 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 the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional analyses may be necessary. These additional efforts are not contained within this method.

2. Summary of Method

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

2.2 This method is suitable for the analysis of waters, soils, or wastes.

2.3 Soil core samples are collected in wide mouth VOC vials with minimum handling to reduce loss of contaminants. Preservation by solvent addition is performed in the lab.

2.4 This method is based in part on 1) USEPA SW-846: the 3rd edition of methods 8000 and 8100; 2) Method OA-2; 3) work by the EPA Total Petroleum Hydrocarbons

Methods Committee; and 4) 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 the chromatographic response falling between the onset of the n-decane (n-C_{10}) peak and the conclusion of the n-octacosane (n-C_{28}) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.

3.2 Diesel Component Standard: A ten component blend of typical diesel compounds (Table 3). This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics.

3.3 Laboratory Control Spike - Water: A reagent water spiked with the Diesel Component Standard and run through the method with water samples as a quality control check. See Section 10.3.1.

3.4 Laboratory Control Spike - Soil: A reagent sand or soil sample spiked with the Diesel Component Standard and run through the method with soil samples as a quality control check. See Section 10.3.2.

3.5 Method Blank - Water: A reagent water sample extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.3 for method blank acceptance criteria.

3.6 Method Blank - Soil: A reagent sand or clean soil extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.4 for method blank acceptance criteria.

3.7 Calibration Check Standard (CCS): A calibration standard analyzed to verify the validity of the calibration curve. See section 10.3.5 for CCS acceptance criteria.

3.8 Temperature Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper cooling of samples has been achieved. A 40 ml or 60 ml vial will be adequate for this purpose.

3.9 Other terms are as defined in SW-846.

4. Interferences

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

4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water and extraction solvent. Method blanks must be analyzed with each batch or for every 20 samples to demonstrate that the analytical system is free of contamination. Contamination limits for blanks can be found in sections 10.3.3 and 10.3.4.

4.3 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 an analysis of a solvent blank to check for cross-contamination.

5. Safety Issues

5.1 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. 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 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.

6. Apparatus and Materials

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph and all required accessories, including a detector, column supplies, recorder, gases, and syringes. A data system capable of determining peak areas and integrating DRO as defined in the method is required.

6.1.2 Columns:

6.1.2.1 Column 1: 25 M x 0.25 mm Quadrex 007 5% methyl phenyl 0.5 micron film thickness.

6.1.2.2 Alternate Column: 30 M x 0.53 mm ID Restek RTX-5, 1.5 micron film thickness.

6.1.2.3 Other capillary columns may be usedprovided they are capable of resolving typical diesel components, and the solvent front from C_{10}.

6.1.2.4 Preference should be given to columns with low bleed characteristics.

6.1.3 Detector: Flame ionization (FID).

6.2 Concentrator tube. Kuderna-Danish - 10 ml graduated (Kontes K-570050-1025 or equivalent). Ground glass stopper is used to prevent evaporation of extracts.

6.3 Evaporative flask, Kuderna-Danish - Attach to concentrator tube with springs.

6.4 Snyder column, Kuderna-Danish - A rotary evaporator may also be used.

6.5 Nitrogen evaporator with high purity nitrogen gas source.

6.6 Analytical balance: A balance capable of accurately weighing 0.0001 g (must be used for standards). A top-loading balance capable of weighing to the nearest 0.1 g (should be used for sample analysis).

6.7 Ultrasonic bath.

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

6.9 VOC Vials and Bottles: Wide mouth 60 ml (2.0 oz.), or 120 ml (4.0 oz.) VOC vials with teflon/silicone septa or teflon lined caps for soils. Amber 1 liter bottles with teflon lined caps for waters.

6.10 Separatory funnel - 2000 ml with Teflon stopcock.

6.11 Microsyringes: 1 ul, 5 ul, 10 ul, 25 ul, and 100 ul.

6.12 Disposable pipets: Pasteur.

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

7. Reagents and Standards

7.1 Reagent Water: DRO free water

7.2 Solvents: hexane, methylene chloride, carbon disulfide - pesticide grade or equivalent. Store away from other solvents. Note: Hexane is the recommended solvent for this method.

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

7.4 DRO free Sodium Chloride - (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.5 DRO free sand or soil

7.6 Surrogates are not mandatory in this method. However, if the laboratory intends to use surrogates, they must be chosen so that they do not elute within the DRO retention time window. Surrogates known to meet this criteria are Nonane (C_9) and Nonacosane (C_{29}).

7.7 Individual Component Stock Standards: Volumetrically prepare individual stock standards for the diesel components in a solvent listed in 7.2 at approximately 20 mg/ml. (Some of the n-alkanes are available in solution in chloroform from Supelco Cat. #4-7102M and 4-7103M.)

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

7.7.2 Using a 100 ul syringe, immediately add 20-30 ul of the diesel component to the flask; then reweigh. The liquid must fall directly into the solvent without contacting the neck of the flask.

7.7.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (ug/ul) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.7.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.7.5 Standards must be replaced after six months unless comparison with unexpired standards documents their accuracy.

7.8 Diesel Component Stock Standard: Commercially prepared diesel component stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source. Diesel Component Stock Standards can be prepared using individual component stock standard solutions. Prepare Diesel Component Standard in a solvent listed in 7.2, as needed, at the concentrations shown in Table 3. These standards must be stored with minimal headspace and must be checked frequently for signs of degradation or evaporation.

7.9 Calibration Standards: Prepare Calibration standards at a minimum of five concentration levels in solvent from the Diesel Component Stock Standard. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC.

8. Sample collection, Preservation, and Handling

8.1 Aqueous samples should be collected in a one liter amber bottle with a teflon lined cap. The Teflon liner must contact the sample. Samples must be preserved with 5 mls of 50% HCl at the time of collection, (acid must be added to the bottle prior to adding the sample). Cool samples to 4°C immediately after collection. Water samples must be held at 4°C and extracted within seven days of collection. Analysis must take place within 47 days of collection. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples preserved with sodium azide or extracted within 48 hours of collection.

8.2 Soils can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore™ sampler or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1. A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination. Care must be taken to be sure the vial seals properly (no soil on the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

8.2.1 Collect and preserve samples by one of the following techniques:

8.2.1.1 Collect soil into tared VOC vials following Table 1. Store samples on ice or at 4°C. Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.

8.2.1.2 Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with teflon sheets placed between the endcaps and the sample. Store samples on ice or at 4°C. Immediately prior to solvent addition, the soil from the brass tube must be subsampled into a VOC vial following Table 1. Subsampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the

appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

8.2.1.3 Pack soil with no headspace into an EnCore™ sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 4°C. Soil stored in the EnCore™ sampler must be extruded from the device into a VOC vial immediately prior to solvent addition. The soil is extruded by using a pushrod supplied with the tool. Soil should not be scooped out of the sampler using a spatula, etc. EnCore™ samplers must be cleaned appropriately (following the manufacturers recommendations) prior to reuse.

8.2.1.4 Alternate sample storage devices equivalent or superior in performance to the brass tube or the EnCore™ sampler may be used for sample storage prior to preservation in the laboratory. Alternate sample storage devices **must be approved** by the Department **prior to use**.

8.2.2 Shipping time should be minimized. Samples must be received by the lab within 72 hours. Refer to Table 2 for soil sample holding times.

8.2.2.1 Extractant solvent must be added to soil vials within 72 hours of sample collection.

8.2.2.2 Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 to determine the volume of solvent to add, or if the sample must be flagged or rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, at the request of clients, the samples must not be reported as "DRO".

8.2.2.3 Add solvent to the sample in a 1:1 ratio (or greater) of mls solvent to grams of sample. Solvent can be injected through the septa, or the vial may be quickly opened to allow the appropriate volume of solvent to poured in. **Solvent must be added to the sample within 72 hours of sample collection**.

8.2.2.4 It is not necessary for the lab to complete the extraction at the time of injection of the solvent (addition of sodium sulfate, sonication, etc.) The date of solvent addition must be reported in lieu of the extraction date. Completion of the extraction (addition

of sodium sulfate, sonication, etc.) need not be done until the time of analysis. Analysis must take place within 47 days of collection.

8.3 Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice". If samples are not "received on ice", temperature shall be determined from:

8.3.0.1 The temperature of an actual sample.

8.3.0.2 The temperature of a temperature blank shipped with samples.

8.3.0.3 The temperature of the melt water in the shipping container.

When no ice is in the cooler, no temperature blank is provided, and there is not sufficient sample volume to sacrifice for a temperature measurement, the laboratory must flag the sample result and state the condition of sample upon receipt (ie. not cooled during shipping, received at room temperature, etc.). **Note: If blue ice packs or similar methods are used, precooling of samples to 4°C with ice or by refrigeration is required.**

9. Procedure

9.1 Samples are analyzed by GC/FID. Waters are extracted using a separatory funnel or continuous liquid liquid extraction technique. Soils are extracted in the vial. Details are given in section 9.5. After the extracts are concentrated, a volume is injected directly onto the GC. The same solvent used for extraction must be used for calibration and analysis. Soil concentrations must be reported on a dry weight basis. The procedure for determination of dry weight can be found in EPA method 5030, section 7.3.3.1.5.

9.2 Gas Chromatography

9.2.1 Conditions: Set column temperature to 60°C for 2 minutes, then 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. Conditions may be altered to improve

resolution of diesel range organics.

9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.3.

9.3 Retention Time Window and Quantitation

9.3.1 The retention time window is defined as beginning approximately 0.1 minutes before the onset of the n-decane peak and ending 0.1 minutes after the conclusion of the n-octacosane peak in the calibration run.

9.3.2 Diesel Range Organics (DRO): Quantitation is based on a direct comparison of the total area within the retention time window to the total area of the Diesel Component Standard. Further instructions on quantitation can be found in section 9.6.

9.3.3 The laboratory must verify the placement of the retention time window at the beginning of each day and whenever a new GC column is installed or when significant retention time shifts occur. This can be accomplished as part of the calibration check.

9.3.4 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of chromatographic graph that includes all responses within the retention time window. The correct baseline placement would a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 is intended to illustrate correct placement of the baseline for several situations.

9.4 DRO Calibration

9.4.1 Run the Diesel Component Standard at a minimum of five concentration levels. One of the concentration levels must be at or near the LOQ. The remaining concentration levels must be evenly distributed within the linear working range of the GC.

9.4.2 Inject each calibration standard. A constant volume of extract must be injected for both samples and standards. Tabulate the entire area (baseline to baseline) for the ten components against the mass injected. Instructions on

baseline to baseline integration can be found in section 9.6. The results are used to prepare a calibration curve by linear regression. The curve must have a correlation coefficient of at least 0.99.

9.4.3 Verify the working calibration curve at the beginning of each working day, by the injection of a Calibration Check Standard (CCS). If the concentration determined from the curve, for the CCS, varies from the known concentration by more than 20%, attempt to correct the problem. If a CCS, run after corrective action has been performed, varies by more than 20% from the known concentration, a new calibration curve must be prepared.

9.5 Sample preparation

9.5.1 Water extraction - Separatory Funnel

9.5.1.1 Check and note the initial pH. If the sample bottles had been supplied by the lab with acid for preservation then this is not required. However, it must be noted somewhere in the report (preferably on the Chain of Custody) that the bottles were supplied this way in lieu of a pH measurement. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifer samples preserved with sodium azide or extracted within 48 hours of collection.

9.5.1.2 Measure a 1-L portion of the sample with a graduated cylinder and transfer to the 2-L separatory funnel. Record the volume. If the sample is in a 1 liter or smaller bottle, the analyst may measure the volume by marking the water meniscus on the side of the sample bottle for later determination. Determine the volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. For blanks and quality control standards, pour 1 liter of reagent water into the separatory funnel.

9.5.1.3 Add 60 mls solvent to the sample bottle to rinse the inner walls (same solvent used for the calibration standards). If a graduated cylinder was used for volume measurement, this must also be rinsed with solvent. Transfer the solvent to the separatory funnel. Add 100 g NaCl to separatory funnel. Extract the sample by shaking it for two minutes with frequent venting to release excess pressure.

9.5.1.4 Allow the layers to separate. Use mechanical techniques to break emulsions if they occur. Mechanical techniques include stirring, filtration through glass wool, and centrifugation.

9.5.1.5 Drain the solvent layer into a 250 ml beaker. If hexane is used for extraction the solvent layer will be on the top.

9.5.1.6 Repeat the extraction once more using a 60 ml aliquot of solvent. Collect the solvent in the same beaker described in 9.5.1.5.

9.5.1.7 Dry extract with Na_2SO_4 and add to Kuderna-Danish (K-D) evaporative concentrator. (The drying step need not be repeated for soil extracts.) Rinse the beaker and the Na_2SO_4 with small amounts of solvent. Add these rinses to the K-D.

NOTE: Equivalent concentration apparatus may be used.

9.5.1.8 Add a boiling chip to the K-D and attach a Snyder to the top. Pre-wet the column by adding about 1 ml of solvent to the top.

NOTE: The concentration step is critical; losses can occur if care is not taken.

9.5.1.9 Place the K-D in a heated water bath set at a temperature appropriate for the chosen solvent so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. When the appropriate volume has been reached, remove the K-D from the bath and allow it to cool completely.

9.5.1.10 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of solvent. Transfer the extract to a calibrated 15 ml centrifuge tube, rinsing with a small amount of solvent. Be sure to rinse all of the ground glass joints well, as compounds collect on the ground glass.

9.5.1.11 Carefully concentrate the extract to 1.0 ml under a gentle stream of nitrogen. The final volume can be greater than 1.0 ml as long as the laboratory can meet the method LOQ. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. Transfer to an appropriate sized vial

with Teflon lined cap, mark the meniscus for final extract volume determination.

9.5.1.12 Record the preparation information for the extraction and concentration steps. The sample extract is ready for analysis in section 9.5.4.

9.5.2 Water extraction - Continuous liquid liquid extraction

9.5.2.1 Mount the continuous extractor on appropriate racks.

9.5.2.2 Put 250 ml solvent in a round bottom flask, add a few boiling chips (same solvent used for the calibration standards). Add 300 ml of solvent to the extractor flask.

9.5.2.3 When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water into either sidearm by pouring the water down the back of the extractor.

9.5.2.4 Check and note the pH. If the sample bottles had been supplied by the lab with acid for preservation then this is not required. However, it should be noted somewhere in the report (preferably on the Chain of Custody) that the bottles were supplied this way in lieu of a pH measurement. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifer samples preserved with sodium azide or extracted within 48 hours of collection.

9.5.2.5 Measure a 1-L portion of the sample with a graduated cylinder and transfer into the extractor flask. Record the volume. If the sample is in a 1 liter or smaller bottle, the analyst may measure the volume by marking the water meniscus on the side of the sample bottle for later determination. Determine the volume by adding tap water to the bottle to the marked level and measuring the volume with a graduated cylinder. Pour the sample into the extractor flask. For blanks and quality control standards, pour 1 liter of reagent water into the separatory funnel.

9.5.2.6 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 on the prep sheet.

9.5.2.7 Remove the condenser from the rack and wipe the lower joint and lip with a tissue soaked with solvent. Place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators.

9.5.2.8 Turn on the heating mantle. Check after 15 minutes to be sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip on the condenser, and that the volume of the solvent in the round bottom flask is still about 240 ml.

9.5.2.9 Check all extractor joints for leaks with a Kimwipe. Allow the extraction to proceed for 18-24 hours.

9.5.2.10 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.

9.5.2.11 The solvent contained in the round bottom flask is the extract. Transfer the extract to a 400 ml beaker, rinsing with a small amount of solvent. If the volume of solvent is less than about 250 ml, record the solvent volume.

9.5.2.12 Go to 9.5.1.7 and proceed with the prep.

9.5.3 Solvent Extraction for Soil/Sediment: This method is based on extracting the sediment/soil with solvent. An aliquot of the extract is concentrated and injected on the GC.

9.5.3.1 Add 25 gms of dried Na_2SO_4 to sample preserved in section 8.2.2.

9.5.3.2 Hand shake sample in its vial vigorously for 2 minutes. Sonicate for 20 minutes. If the sample is not well mixed then stir the mixture with a steel spatula, shake for 2 minutes and resonicate.

9.5.3.3 Allow sediment to settle until a layer of solvent is apparent.

9.5.3.4 Decant the solvent or remove with a syringe into a 150 ml beaker.

9.5.3.5 Repeat extraction once more and combine the extracts.

9.5.3.6 Go to 9.5.1.7 and proceed with the prep.

9.5.4 Inject an appropriate volume of concentrated extract onto the GC and proceed with the analysis. A constant volume of extract must be injected for both samples and standards. If the sample response exceeds the calibration range for the DRO an appropriate dilution should be used. An appropriate dilution is one that keeps the response (both area and peak height) of major constituents in the upper half of the calibration range. If an initial dilution does not accomplish this then an intermediate dilution should be performed.

9.6 Calculations:

9.6.1 DRO Calibration: Quantitation of DRO is performed by the external standard method. The concentration of Diesel Range Organics in the sample is determined from a summation of the total response within the range of the elution of n-decane and n-octacosane, using the calibration curve. No area may be subtracted from the DRO retention time window in calculating DRO results.

9.6.1.1 Integration must be "baseline to baseline" as opposed to a "valley to valley". Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The correct baseline coincides with a horizontal line drawn through the lowest point in the chromatogram before the end of the window. The lowest point may be within the window, before the window, or before the solvent front. Baseline to baseline integration does not include the solvent peak. Placement of the baseline is determined for each sample. Figure 1 illustrates correct placement of the baseline for several chromatograms.

9.6.1.2 Refer to Section 9.3, Retention Time Windows and Quantitation, for information on establishing the retention time window. From linear regression of calibration standard GC responses (R) against their known concentrations (C in ug/ml) 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 sample in ug/l for waters and mg/kg on a dry weight basis for soils

m = slope of the calibration curve

R_s = GC response of sample in the DRO retention time window

b = intercept of calibration curve

V_E = total volume of sample extract (after concentration) in ml

V_s = volume of water sample in liters

D = dilution factor if extract was diluted

W = total dry weight of soil sample in gm

9.6.2 Peak areas measured from blanks may not be subtracted from sample peak areas. All blank concentrations (above the LOD) must be reported. Sections 10.3.3 and 10.3.4 give acceptance criteria for blanks. Blank concentrations up to and including the acceptance criteria must be reported. Blank concentrations exceeding the acceptance criteria require reanalysis.

9.6.3 Report the presence of significant peaks outside the chromatographic window. Significant peaks are peaks which can be distinguished above the noise in a chromatogram. Any peak 3 times the standard deviation of the signal to noise ratio is statistically significant. To accommodate heavier oils and to insure that peaks outside the DRO window are not missed, run the chromatogram out 5 minutes past the last component in the DRO component

standard. All peaks (and baseline rises) outside the window are to be reported. If area outside the window is detected it must not be quantitated as part of the DRO result. Laboratories may quantitate this area outside the window against the DRO standard and report a concentration detected outside the window or simply report that peaks or baseline rises were detected outside the window.

9.6.4 All area detected in the DRO window must be reported as "DRO". Reporting "nonpattern match", "nonapplicable", "nonpetroleum" etc. will not be acceptable. If the Consultant or RP feel that the DRO result does not represent contamination at the site, for example, if they wish to attribute the DRO detection to naturally occurring organics then confirmation by mass spectroscopy will be required. For further information on MS confirmation see the "LUST and Petroleum Analytical and Quality Assurance Guidance", #PUBL-SW-130, most recent revision, (Section 8.0, Soil Analytes Table, footnotes).

10. Quality Control

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

10.1.1 Replicate Laboratory Control Spike - Water: Analysis of 5 replicates at a concentration of 100 ug/l. Recoveries must fall between 75%-115% of the known concentration and the RSD must be <20%.

10.1.2 Replicate Laboratory Control Spike - Soil: Analysis of 5 replicates at a concentration of 10 mg/kg. Recoveries must fall between 70%-120% of the known concentration and the RSD must be <20%.

10.2 The laboratory must determine its LOD and LOQ for both soils and waters. The LOD determination must be performed in accordance with 40 CFR, Part 136, Appendix B. Soil LODs are performed in accordance with 40 CFR, Part 136, Appendix B using a DRO free sand or soil, and the same extraction method used for soil samples. The LOQ calculation can be found in "Principles of Environmental Analysis", Analytical Chemistry, Vol. 55, No. 14, December 1983, 2210-2218. The LOQ is defined as:

$$LOQ = 10(S)$$

Where S is the standard deviation determined from analysis of seven replicate spikes analyzed to determine the LOD in accordance with 40 CFR, Part 136, Appendix B.

10.3 With every batch of 20 samples or less the lab must analyze:

10.3.1 Duplicate Laboratory Control Spike - Water : The Duplicate LCS-water must be processed through the method in the same manner as water samples. The recovery of the LCS-water spikes must be between 75%-115% and the RPD<20%. The LCS-water must be run with every batch of 20 water samples. One of the LCS-waters must be run at the beginning of a batch of samples and the other at the end.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

10.3.2 Duplicate Laboratory Control Spike - Soil : The Duplicate LCS-soil must be

run through the method in the same manner as soil samples. The recovery of the LCS-soil spikes must be between 70%-120% and the RPD<20%. The LCS-soil must be run with every batch of 20 soil samples. One of the LCS-soils must be run at the beginning of a batch of samples and the other at the end.

Note: If samples are reanalyzed in a subsequent "batch" because the original sample was not appropriately diluted, it is not necessary to rerun the LCS with the diluted sample. This allowance only applies if the LCS run with the sample initially was in control, and the same initial calibration curve is being used. All other QA requirements still apply.

10.3.3 Method Blank - water: The method blank - water must be processed through the method in the same manner as water samples. If the concentration exceeds 50 ug/l, all water samples associated with this blank (samples run since the last blank that was below 50 ug/l) must be rerun.

10.3.4 Method Blank - soil: The method blank - soil must be processed through the method in the same manner as soil samples. If the concentration exceeds 5.0 mg/kg, all soil samples associated with this blank (samples run since the last blank that was below 5.0 mg/kg) must be rerun.

10.3.5 Calibration Check Standard (CCS): The CCS response must be within $\pm$ 20% of the value predicted by the curve or a new curve must be generated. The CCS must not be used to update the curve or used in any other manner for quantitation.

10.4 The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99.

10.5 If any of the criteria above are not met, the problem must be corrected before further samples are analyzed. Any samples analyzed between the last QC samples that meet the criteria and those that have fallen out must be rerun. If this is not possible, affected sample results must be flagged.

10.6 Solvent blanks should be run after samples suspected of being highly concentrated to prevent carryover.

10.7 Standard diesel fuel and other heavy end fuel mixtures are available commercially if the laboratory desires additional performance indicators.

11. Method Performance

11.1 The required Limit of Quantitation (LOQ) is 10 mg/kg or less for soils and 0.1 mg/l or less for waters. A chromatogram for the Diesel Component Standard is in Figure 2.

12. References

0.1 USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 8000, 8100, 3510, 3520, 3540, and 3550.

2. "Method OA-2: Extractable Petroleum in Products", Revision January 10, 1990; University Hygienic Laboratory, Iowa City, Iowa.

3. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water" - Draft - February 28, 1990; prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.

4. Silis, K., M. McDevitt, and J. Parr; "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment", presented at the conference on Petroleum Hydrocarbons and organic Chemicals in Groundwater, NWWA, Houston, Texas, November 1988.

5. "Leaking Underground Fuel Tank (LUFT) Field Manual", State Water Resources Control Board, State of California, Sacramento, CA, May 1988.

6. Fitzgerald, John; "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure", Petroleum Contaminated Soils, Vol. 2, 1989.

7. Senn, R.B., and M.S. Johnson; "Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigation", Ground Water Monitoring Review, 1987.

8. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" presented at 5th Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989.

9. ASTM "Standards Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," 3328-78.

Table 1
Weight Maxima

Vial Size	Target Sample Weight	Actual Sample Weight	Minimum Volume of Solvent	Action
60 mls	25 gms	<25 gms	25 mls	Adjust MDL
		25-35 gms	≥25-35 mls	Add Solvent
		>35 gms	for any amount	Reject
120 mls	25 gms or 50 gms	<25 gms	25 mls	Adjust MDL
		25-70 gms	≥25-70 mls	Add Solvent
		>70 gms	for any amount	Reject

Laboratories should use standard rounding rules to determine compliance with the maximum weight requirement. Sample weights should be rounded to the nearest whole number. This means that a sample weighing between 34.5-35.4 is rounded to 35.0 gms, and a sample weighing between 69.5-70.4 gms is rounded to 70.0 gms. There will be NO allowances given past these tolerances.

Table 2
Sample Holding Times and Storage

Analysis Method	Sample Storage	Holding Times from Date and Time of Collection			
		Solvent Addition	Shipping	Extraction	Analysis
DRO waters	Amber Bottle	NA	7 days	7 days	47 days
DRO carbonate aquifers	Amber Bottle	NA	2 days unless azide preserved	2 days unless azide preserved	47 days
DRO soils	VOC vial	within 72 hours	72 hours	47 days	47 days
	Brass Tube or EnCore™	within 72 hours	72 hours	47 days	47 days

Table 3

DIESEL COMPONENT STANDARD AND CONCENTRATIONS	
Component	Concentration, ug/ml
Decane	1000
Dodecane	1000
Tetradecane	1000
Hexadecane	1000
Octadecane	1000
Eicosane	1000
Docosane	1000
Tetracosane	1000
Hexacosane	1000
Octacosane	1000
Total	10,000

Note: The concentration of the Diesel Component Standard may be varied as long as the concentration of each component is the same.

Figure 1
Integration Examples

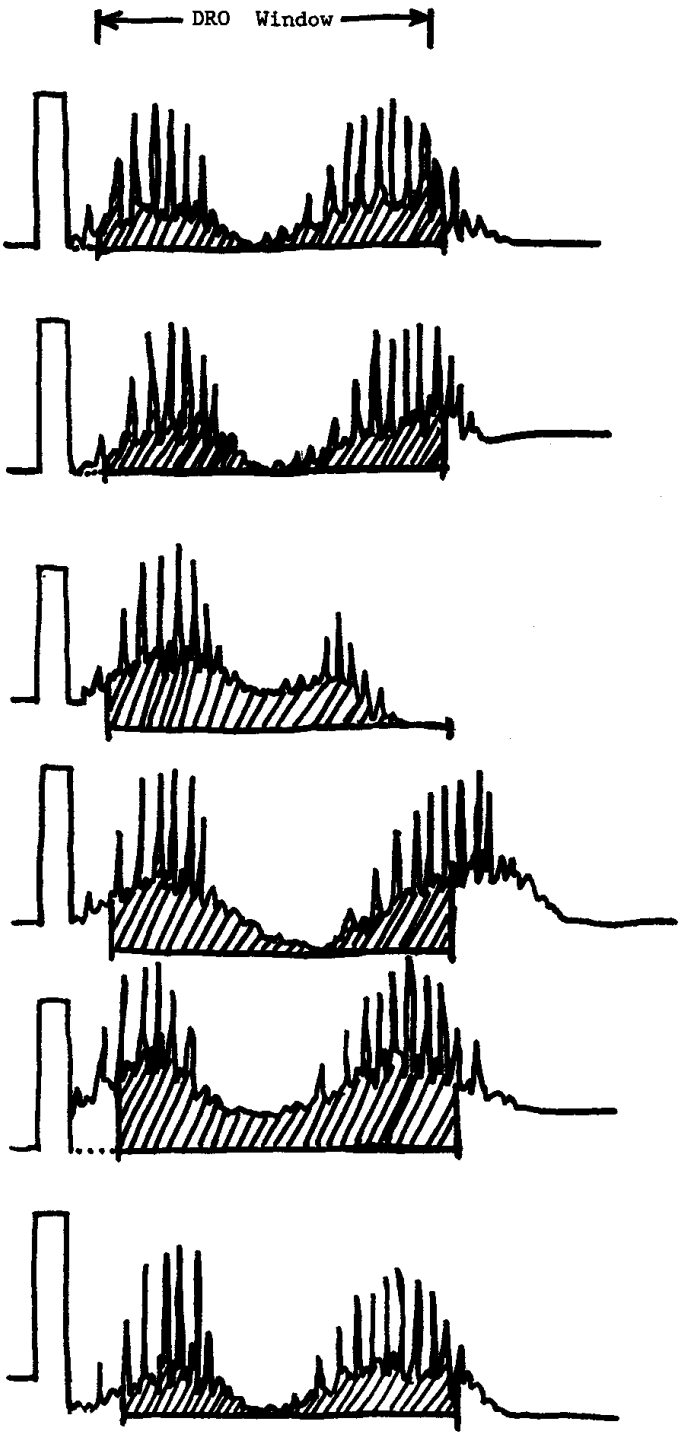

FIGURE 2

Diesel Component Standard