METHOD 8640

DIESEL RANGE ORGANIC HYDROCARBONS IN WATER AND SOIL USING ULTRAVIOLET FLUORESCENCE (UVF) WITH SOLVENT EXTRACTION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts formally trained in the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique, which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. Performance data included in this method are for guidance purposes only and must not be used as absolute quality control (QC) acceptance criteria for the purposes of laboratory QC or accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method uses ultraviolet fluorescence to determine the concentrations of Diesel Range Organics (DRO) from C10 to C28 plus Oil Range Organics (ORO) from C28 to C36 to measure Extended Diesel Range Organics (EDRO) from C10 to C36. This method cannot distinguish these individual carbon ranges and for the purpose of this document evaluation of C10 to C36 is cited as DRO and EDRO, interchangeably. Specifically, this method detects polycyclic aromatic hydrocarbons only, with no or little sensitivity to monoaromatic hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylenes) below the C10 carbon weight.

1.2 This method can be used to quantitate hydrocarbons that are soluble in methanol, hexane, or other suitable solvents provided that the desired performance data can be generated.

1.3 This method is not appropriate for the quantitation of individual compounds, unless the contaminant in the sample matrix only contains one compound. In most cases, DRO contaminated samples contain many polycyclic aromatic compounds which co-fluoresce with UVF instrumentation. If analyzing individual analytes is required, refer to Method 8000 or Extractable Petroleum Hydrocarbon (EPH) Methods using gas chromatography instrumentation for guidance.

NOTE: Fluorescence-based instruments are not sensitive to aliphatic hydrocarbons.

1.4 Choosing the appropriate calibration standard is dependent on the type or age of petroleum suspected in a sample. Results may be biased low or biased high depending on which standard is used for calibration and analysis. In general, DRO content in fuels and oils can vary considerably and include a large number of refined petroleum products (e.g. gasolines, diesel fuels) and unrefined petroleum products (e.g. heavy fuel oils, crude oils). Since DRO is typically used for underground storage tank (UST) releases, this method was developed using commercially available certified reference standards suitable for most UST applications based on historical performance data compared to laboratory GC methods. Unlike GC methods, since UVF does not quantitate hydrocarbons using retention times, is not sensitive to aliphatic

hydrocarbons and cannot detect individual compounds, this method is intended for screening purposes.

1.5 This method is used with Method 8630 for Gasoline Range Organics (GRO) analysis to evaluate Method 8650 for Total Petroleum Hydrocarbon (TPH), by adding the DRO and GRO concentrations in a sample together to report TPH. This method was validated by U.S. EPA for TPH measurement in soil. See Reference 1 in Sec. 16 for guidance. North Carolina Department of Environment and Natural Resources (NCDEQ) approved this method for soil analysis at petroleum sites, requiring DRO and GRO analysis be performed to report TPH. Regulatory guidelines from 2017 are shown in Figure 1. See Table 3 in Reference 2, Sec. 16 for updated guidelines.

1.6 Prior to employing this method, analysts are advised to consult the manufacturer's instructions for additional information on QC procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this method is provided by the Environmental Protection Agency (EPA) as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives (DQOs) for the intended application

2.0 SUMMARY OF METHOD

2.1 Samples are extracted in solvent for analysis by UVF using the appropriate sample preparation procedures specified by each manufacturer's UVF instrument or refer to Method 3500 for alternative sample preparation methods.

2.2 DRO in samples can be measured using UVF instruments fitted with appropriate excitation and emission optical filters and ultraviolet light sources. Sensitivity varies depending on the types and quantities of polycyclic aromatic hydrocarbons in a sample. In general, this method detects hydrocarbons in the C10 – C36 carbon range.

2.3 This method is intended for both laboratory and field use. Refer to Method 8000 for additional calibration and quality control procedures for further guidance. Use of surrogates and surrogate recovery analysis is not used with this method.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences during sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on glassware cleaning.

4.2 Raw data from all blanks, samples and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and take corrective action to eliminate the problem. Subtracting method blank values from sample results is not permitted. If measured concentrations are suspected of being biased or false positive results for a sample, the laboratory should qualify the affected data or otherwise inform the data user(s) of any suspected data quality issues.

4.3 Contamination from carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the glass cuvette used for analysis must be rinsed with solvent between sample measurements. Fill the cuvette with solvent and test a blank to check for contamination. Rinse again with solvent or use a new cuvette if measurements are elevated.

4.5 Phthalates in plastic laboratory supplies can extract in solvent and elevate results. Use glass, plastics coated with polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) or use testing supplies provided by the manufacturer.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section lists laboratory glassware and supplies used to develop this method. Other, alternative supplies not listed may be used. Refer to each manufacturer’s product for guidance.

6.1 Ultraviolet Fluorescence (UVF) spectrophotometer

An analytical system (e.g., fluorometer) equipped with a UV light source, excitation filter, emission filter, detector, and glass cuvette or sample cell. This includes fixed-wavelength fluorometers, multi-wavelength scanning fluorometers and laser induced fluorescence (LIF)

technologies. The analyzer must be fitted with suitable components for the intended application.

6.2 UVF instrument configurations

The choice of components will depend on the analytes of interest, the expected concentrations, and the intended use of the results. Commercially available fixed-wavelength analyzers with configuration listed in this section were used to develop the method and are not intended to exclude the use of other instruments configured differently or that may be developed. Laboratories may use other UV light and optical filter components provided that the laboratories document method performance data that are appropriate for the intended application.

Configuration for DRO - Use a 255-nm LED, 254-nm mercury vapor lamp or similar UV light source at this wavelength, fitted with a 254-nm peak transmission narrow band excitation filter and a 350-nm broad band emission filter. Use of square quartz glass cuvettes is required.

6.3 Data system

A computer system that allows the continuous acquisition and storage of raw data recorded by the analyzer. UVF instruments that do not have computer connection capability must, at a minimum, provide output of raw data (fluorescence response or voltage) and/or concentration to record manually.

6.4 Digital balance, 0.1-g capacity or lower.

6.5 High precision adjustable micro pipette, 25 µL to 250 µL capacity.

6.6 Soil extraction jars, 30 mL capacity, HDPE plastic with wide mouth screw cap.

6.7 Water extraction vials, 40 mL capacity with or without 5 mL graduations, clear glass, with PTFE-lined screw cap.

6.8 Storage vials, 5 mL capacity or larger, clear glass with PTFE-lined cap.

6.9 Syringes, 5 mL capacity or larger, glass or polypropylene plastic with Luer lock.

6.10 Syringe filters, 0.45 µm size, PTFE-lined plastic with Luer lock.

6.11 Graduated cylinders, 5 mL, 10 mL or higher capacity with 1 mL graduations, glass, or polypropylene plastic.

6.12 Volumetric flasks, 5 mL, 10 mL or higher capacity, glass.

6.13 Solvent dispenser or squirt bottle, PTFE or FEP lined solvent resistant plastic.

6.14 Tissue wipes, lint free, laboratory grade.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade HPLC solvents, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where specifications are available. Other grades may be used, provided the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent leaching of contaminants from plastic containers.

7.2 Extraction solvents

This method has been validated using the solvents listed below. Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix, at the concentrations of interest. The choice of extraction solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, including those specifically listed in this method, the analyst must demonstrate adequate performance for the analytes of interest, at the desired project-specific concentration levels. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

Matrix:	Solvent:	CAS No.
Soil, sediment, most other solid samples	Methanol, Methyl Alcohol or other polar solvents	67-56-1
Fresh or salt water, groundwater, other aqueous samples	Hexane, n-Hexane or other non-polar solvents	110-54-3
Oils, Fuels, Sludges, Wastes or Non-Aqueous Phase Liquids (NAPL)	Hexane or use methanol if appropriate	

CAUTION: Avoid using dichloromethane (DCM or methylene chloride) solvent for soil extraction and analysis. DCM may damage square cuvettes. Use hexane if a more powerful solvent is preferred. Keep in mind the moisture content in soils or sediments may inhibit extraction efficiency with hexane.

7.3 Calibration standards – A minimum of five different concentrations for each parameter of interest should be prepared and used for instruments that can perform multi-point calibrations. If the instrument cannot, then calibrate using a single-point standard and a blank as indicated in Sec. 11.1.2. Calibration standards should be replaced after the manufacturer's expiration date or sooner if comparison with check standards indicates a problem. See Method 8000 for additional information on the preparation of calibration standards. Use standards specified below. Consult with the UVF manufacturer for guidance.

7.3.1 Primary calibration standard – Use to establish baseline DRO measurement. Use conventional No. 2 diesel fuel, CAS# 68334-30-5 only, with a medium boiling point range of 170°C to 430°C, as defined in Method 8015, Sec. 1.2.2.

Use for DRO analysis if the suspected source of hydrocarbons is fresh and not weathered (e.g. from a recent UST spill). Use this fuel type by default to report DRO in samples if the source of hydrocarbons is unknown.

7.3.2 Secondary calibration standard – Use a certified 50% weathered No. 2 diesel fuel, formulated using CAS# 68334-30-5, for DRO measurement if the suspected source of hydrocarbons is weathered or degraded (e.g. from an old UST spill) or for heating oils, heavy fuel oils and crude oils with high boiling point ranges >430°C. These contaminants and the weathered diesel standard contain a higher composition of aromatic hydrocarbons and fluoresce stronger compared to fresh No. 2 diesel fuel. As a result, when used to calibrate, the 50% weathered diesel standard produces lower sample readings and will perform better if results are biased high using the fresh No. 2 diesel fuel standard. Choose a CRM which produces sample readings 1.5 to 2 times lower compared to the baseline DRO measurement.

7.3.3 Project-specific calibration standard – Use alternative standards when appropriate, including DRO standards supplied by proficiency testing providers to perform DRO proficiency studies, for calibration and analysis.

7.4 Blanks – Three types of solvent blanks are necessary for analysis: (1) the calibration blank, which is used in establishing the calibration curve; (2) the method blank, which is used to monitor for possible batch contamination resulting from the sample preparation procedure; and (3) the rinse blank, which is used to flush the cuvette between all samples and standards. See Sec. 11.6 for frequency for analyzing rinse blanks.

7.5 As with the equipment and supplies, each commercially available testing product will supply or specify the reagents necessary for successful completion of the test. This includes the calibrators (standards) and solvents to use. Detailed information on reagent requirements is given in the manufacturer's literature. Store all reagents and standards according to the manufacturer's instructions, and, where applicable, discard any that are past the expiration date assigned by the manufacturer.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation, and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation, and storage requirements.

8.1 See the introductory material to Chapter Four, "Organic Analytes" for storage conditions and holding times.

8.2 Store the sample extracts at ≤6 °C (protected from light) in glass vials equipped with PTFE-lined screw caps.

9.0 QUALITY CONTROL

9.1 General Guidance

Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Also, refer to Chapter One for additional guidance on quality assurance (QA) and QC protocols that may be applicable. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those implementing the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged as described in Sec. 9.5. Use of instrument specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific determinative method QC procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation techniques. These methods were developed for gas chromatography analysis, but apply with this method in some cases. Some QC procedures may not be practical for use in field. Use for guidance purposes only.

9.3 Initial demonstration of proficiency (IDP)

The initial demonstration of method proficiency must be performed by the laboratory prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure, and change in analyst). Refer to Method 8000 Sec. 9.0 for additional information regarding instrument, procedure, and analyst IDPs. An IDP must consist of replicate reference samples from each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix taken through the entire preparation and analysis.

9.4 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation, if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such “blank subtraction” may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.5 Sample QC for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch of up to 20 field samples. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair for up to 20 field samples. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, laboratories may use a matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, then laboratories should use a matrix spike and matrix spike duplicate pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.5.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked into a clean matrix with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike are not within control, the LCS results are used to verify whether this issue is due to laboratory performance or due to the matrix. Recovery issues in the LCS can indicate possible issues with the entire analytical batch. Consult Method 8000 for information on developing LCS acceptance criteria.

9.5.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.6 Linear range

The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the highest standard in the calibration. The standard must recover within 10% of the true value and if successful establishes the linear range. The linear range standards must be analyzed in the same instrument run as the calibration they are associated with (i.e. analyzed on a daily basis) but may be analyzed anywhere within that run. If a linear range standard is not analyzed for any specific analyte, the highest standard in the calibration becomes the linear range.

9.7 Lower Limit of Quantitation (LLOQ) check standard

The laboratory must establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. LLOQ verification is recommended for each project application to validate quantitation capability at low analyte concentration levels. This verification may be accomplished by spiking either a clean control material (e.g., reagent water, solvent blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix, free of target compounds at the LLOQ and processing through all preparation and determinative steps of the method. Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated Data Quality Objectives (DQOs).

9.7.1 Determination of LLOQs using spiked clean control material represents a best-case scenario and does not evaluate potential matrix effects of real-world samples. For application of LLOQs on a project-specific basis with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.7.1.1 A LLOQ check standard (not part of an initial calibration) is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. The LLOQ check is carried through the same preparation procedures as the environmental samples and other QC.

9.7.1.2 Recovery of target analytes in the LLOQ check standard should be within established in-house limits, or other such project-specific acceptance limits, to demonstrate acceptable method performance at the LLOQ. Until the laboratory has sufficient data to determine acceptance limits, LCS criteria having percent difference (%D) values of ≤20% may be used for the LLOQ acceptance criteria. This acknowledges the poorer overall response at the low end of the calibration curve. Historically-based acceptance criteria should be determined as soon as practical once sufficient data points have been acquired.

9.7.1.3 In-house acceptance criteria for recovery of the LLOQ check standard for a particular sample matrix can be calculated when sufficient data points exist. The laboratory should have a documented procedure for establishing in-house acceptance ranges; if the lower limit of the acceptance range is calculated to be <10%, it should be set to 10%. However, an alternative lower acceptance limit may be established by the laboratory or set at the project level through the DQOs in a QAPP.

9.8 Fluorescence quenching

Samples too high in concentration may quench or swamp the detector, producing low, non-linear measurements. This can occur when testing extracts without diluting the extract prior to analysis. Check for sample quenching by testing the extract at multiple dilutions, typically two or more as needed and multiply the readings by each dilution factor to compare the concentrations in the sample. Ideally, report sample results with readings between the LLOQ and the linear range of the calibration. Dilutions with readings below the LLOQ are too low and should not be used to calculate the final concentration. Dilutions with readings above the linear range are too high and are likely more susceptible to quenching. If the relative percent difference (RPD) between duplicates or percent relative standard deviation (%RSD) for more

than 2 results is ≤20%, the average concentration of these results is reported as the final concentration in the sample.

NOTE: Heavy fuel oils, crude oils, coal tars or other samples high in PAH content will quench more than gasoline, diesel or other refined petroleum products low in PAH content.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.1 for information on calibration and standardization.

11.0 PROCEDURE

Set up the UVF with the proper optical configuration and calibration solutions following the manufacturer's instructions. Prepare calibration solutions in the same solvent used for sample analysis. Use the pipette, volumetric flasks, and glass storage vials in Sec. 6.0 to prepare stock solutions and calibration standards. Select and use commercially available Certified Reference Materials (CRMs) appropriate for analysis or use standards provided with each manufacturer's product, if available. Establish operating parameters that provide instrument performance appropriate for the intended application.

11.1 Initial calibration

11.1.1 For each analysis of interest, prepare Initial Calibration (ICAL) standards at a minimum of five different concentrations. One of the standards should be at a concentration at or below the LLOQ necessary for the project (based on the concentration in the final volume described in the preparation method, with no dilutions). The concentrations of the other standards should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

11.1.2 Calibrate UVF to a multi-point curve using the standards and a solvent blank following manufacturer's instructions. For instruments which can only perform a single-point calibration, use the highest concentration standard and a solvent blank to calibrate. Analyze the four other standards to record the response.

11.1.3 Record and calculate the calibration factors (CF) to establish the fluorescence response in the calibration curve. Fluorescence response may be voltage, raw fluorescence units (RFU), percent fluorescence scale (%FS) or other output from the instrument.

$$\text{Calibration Factor} = \frac{\text{Standard Response} - \text{Solvent Blank Response}}{\text{Standard Concentration}}$$

11.2 Calibration linearity

The linearity of the calibration must be assessed. This applies to both single-point and multi-point calibration curves.

11.2.1 If the percent standard deviation (%RSD) of the calibration factor is ≤20% over the working range, then linearity through the origin can be assumed, and the average calibration factor can be used in place of the calibration curve.

11.2.2 If the %RSD is >20% over the working range, linearity through the origin cannot be assumed. See Method 8000 for other calibration options that may be employed, which may include: a linear calibration not through the origin or a non-linear calibration model (e.g., a polynomial equation).

11.3 Calibration verification

Calibration check analyses are used to assess calibration drift and memory effects over time for each analytical system. Verification is accomplished by the measurement of a hydrocarbon standard on the calibration curve. These analyses may include a span (low and high) to cover the full calibration range, or mid-range concentrations using the ICAL standards or a Continuing Calibration Verification (CCV) standard made from the same stock solution as the ICAL standards. If reusing ICAL or CCV standards for analysis, pour back into glass vials after use and follow the manufacturer's instructions for storage and shelf life.

11.3.1 CCV standard must be analyzed in the beginning of each 12-hour analytical period prior to any sample analysis using the technique and conditions used for analysis of ICAL standards and samples.

11.3.2 Calculate the percent difference (%D) for the CCV standard response compared to the ICAL response. If the response is within ±20% of the response obtained using the initial calibration CF, then the initial calibration is considered still valid, and the analyst may continue to use the mean CF values from the initial calibration to quantitate sample results. If the response varies from the predicted response by more than ±20%, corrective action must be taken to restore the system or a new calibration curve must be prepared for analysis.

11.4 Second source standard

Prior to analyzing samples, verify the ICAL using a standard obtained from a second source to the calibration standards, if possible, such as a second manufacturer or a manufacturer's batch prepared independently from the batch used for calibration, if readily available. Suggested acceptance criteria for the analyte concentrations in this standard are 70 – 130% of the expected analyte concentration.

11.5 Laboratory control sample standard

LCS standards may also serve as the CCV and should be prepared and analyzed concurrently with the samples. Calculate the LCS concentration using the ICAL CF and if the response is within ±20% (or within 80 – 120% recovery) of the true value of the LCS, then the initial calibration is considered still valid, and the analyst may continue using the mean CF values from the initial calibration to quantitate sample results. If the response varies from the predicted response by more than ±20%, corrective action must be taken to restore the system or a new calibration curve must be prepared for analysis.

11.6 Solvent blanks

Solvent blanks or rinse blanks must be analyzed routinely before and after the CCV and prior to samples in order to ensure that the total system (i.e., solvent, cuvette) is free of contaminants.

11.7 Method blanks

Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment and laboratory supplies used in contact with the sample and reagents are assessed for background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. Prepare the method blank using an interference-free blank matrix, similar to the sample matrix, to which all reagents are added in the same volumes or proportions as used in sample preparation. For aqueous analyses, analyte-free reagent water is typically used. For soil analyses, a purified solid matrix (e.g., sand) is typically used. Method blank results should be evaluated in conjunction with other QC information to determine the acceptability of the data generated for that batch of samples. The method blank results should be below the LLOQ for the target analytes being tested; otherwise, corrective action should be taken.

11.8 Water sample extraction and analysis

Add 15 mL of water to a 40 mL glass VOA vial. Add 15 mL hexane to vial to create a 1:1 extract. Tighten cap and shake by hand to mix contents for a minimum of 2 minutes. Let extract settle for several minutes to separate the hexane and water layers. If extracts are dirty and require filtration, use a syringe and syringe filter to remove particulates in the extract prior to use. If this is performed, QC samples in the analytical batch should also undergo filtration. Store filtered extracts in a glass extract vial. Pour the extract into a glass cuvette, clean the outside of the cuvette with a tissue wipe and insert into UVF for measurement. Prepare and test dilutions using the extract as necessary with a micro-pipette and volumetric flask or graduated cylinder.

11.8.1 Diluted extracts – Use more solvent with less water. Use 20 mL of hexane extracted with 10 mL of water to create a 2:1 diluted extract. Multiply sample readings by 2 to calculate final concentration in sample if diluted extract is used for analysis.

11.8.2 Concentrated extracts – Use more water with less solvent. Use 10 mL of hexane extracted with 20 mL of water to create a 1:2 concentrated extract or use 5 mL of hexane extracted with 25 mL of water to create a 1:5 concentrated extract. Divide sample readings by 2 or 5 to calculate final concentration in sample if concentrated extract is used for analysis.

11.8.3 Emulsified extracts – Allow extra time for the solvent and water to separate if solvent layer in extract is emulsified. Filtering the extract may be required to correct the problem or prepare a new sample using a diluted extract.

11.9 Soil sample extraction and analysis

Weigh sample into a 30 mL plastic jar or use a 40 mL glass VOA vial and add methanol using the weights and volumes listed below. Tighten the cap and shake by hand to mix contents for a minimum of 2 minutes. Let extract settle for several minutes afterward for solids to

separate. Use a syringe and syringe filter to remove particulates prior to analysis. If extract is difficult to filter, prepare a more diluted extract. Pour the extract into a glass cuvette, clean the outside of the cuvette with a tissue wipe and insert into UVF for measurement. Store filtered extract in a glass vial. Prepare and test dilutions using the filtered extract as necessary with a micro-pipette and volumetric flask or graduated cylinder.

11.9.1 Undiluted extracts – Use 10-g (±0.1-g) of sample with 10 mL of methanol to create a 1:1 extract. If the undiluted extract is used for analysis, no dilution factor is applied to the final concentration. Prepare dilutions to the extract for analysis as needed.

11.9.2 2X Diluted extracts – Use 10-g (±0.1-g) of sample with 20 mL of methanol or use 5-g (±0.1-g) of soil with 10 mL of methanol to create a 2:1 diluted extract. Multiply sample readings by 2 to calculate final concentration in sample if diluted extract is used for analysis. Account for the 2X dilution factor when preparing additional dilutions for analysis.

11.9.3 4X Diluted extracts – Use 5-g of soil (±0.1-g) with 20 mL of methanol to create a 4:1 diluted extract. Use for clay or other highly absorbent soils which take a long time to settle and difficult to filter unless more solvent is used for extraction. Multiply sample readings by 4 to calculate final concentration in sample if diluted extract is used for analysis. Account for the 4X dilution factor when preparing additional dilutions for analysis.

11.9.4 10X or 20X Diluted extracts – Use for highly contaminated homogenous matrices, including sludges or oily samples. Use 2-g of sample (±0.1-g) with 20 mL of methanol to create a 10:1 diluted extract or use 1-g of sample (±0.1-g) with 20 mL of methanol to create a 20:1 diluted extract. Account for the 10X or 20X dilution factor when preparing dilutions for analysis.

11.9.5 Sediment samples – If samples are wet, the water content in the sample should be minimized prior to use. Decant water from the sample collection jar and use a 5-g or 10-g aliquot for extraction. If results are to be corrected for percent dry weight, use the leftover decanted sample contents for dry weight analysis.

11.9.6 Extraction time – Some matrices may require longer extraction time to improve extraction efficiency. Prior to filtering, allow sample to extract for 1 hour or up to 24 hours, periodically shaking the extract. This may not be practical when testing samples in the field.

11.9.7 Centrifuging extracts – May be used as an alternative to filtering extracts provided the extract is clear of particulates which may cause interference in readings.

11.10 Determination of percent dry weight

When sample results are to be calculated on a dry weight basis, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

11.10.1 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5- to 10-g aliquot of the sample to the nearest 0.01 g into a tared crucible. Dry this aliquot overnight at 105 °C. Allow to cool in a desiccator before weighing.

11.10.2 Calculate the % dry weight as follows:

$$\%\ \text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}}\ \text{x}\ 100$$

This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

11.11 Quantitation

The concentration of hydrocarbons in the sample is measured on the calibration curve and recorded by the instrument. Report sample readings within the linear range of the curve. When sample extracts are prepared and analyzed at different dilutions, the readings should have RPD or %RSD (comparing more than 2 replicates) ≤20%. Report the average concentration. If the RPD or %RSD in sample results is >20%, the sample may be quenching the detector or an error occurred preparing the dilution. The analyses should be performed again.

11.12 Instrument maintenance

Refer to each manufacturer's product for instrument maintenance instructions.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.11. Refer to the manufacturer's instructions regarding data analysis and data calculations. Results need to be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data does not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. Performance data must not be used as absolute QC acceptance criteria for laboratory QC or accreditation.

13.2 In the case of this method (which may be used in either the field or the laboratory), any test kits used must be able to meet the performance specifications for the intended application. However, required performance criteria for a particular testing product may be included in the manufacturer's instructions.

13.3 Table 1 shows fluorescence of Certified Reference Materials (CRMs) used to establish baseline DRO measurement as specified in Sec. 7.3 and 11.4. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2, testing samples at 10 ppm concentrations using two calibrations. Calibration 1 was performed using AccuStandard, Inc. p/n FU-009-40X supplied in methanol. Calibration 2 was performed using Sitelab Corporation EDRO standard p/n CAL-042M in methanol, containing 50% weathered No. 2 diesel fuel. The two calibration standards contain different compositions of aromatic hydrocarbons. In this case, fresh, unweathered No. 2 diesel fuel fluoresces weaker compared to 50% weathered diesel fuel. As a result, sample readings are always about 1.6 to 1.7 times higher or lower depending on which calibration is used. This ratio is within the range specified in Sec. 7.3.2. Other AccuStandard CRMs made from the same fuel source were analyzed and percent difference (%D) values are close to 100% compared to the Calibration 1 response and are suitable to establish baseline DRO measurement. Alternative CRMs made by Restek Corporation were analyzed and fluoresced weaker in Calibrations 1 and 2, but ratios exhibited are within the 1.5 – 2x ratio limit and the two percent difference values meet the 70 – 130% acceptance limit, which qualifies these products as second source calibration standards. To achieve this, Restek's 75% weathered diesel fuel had to be used. For comparison, AccuStandard's 75% weathered diesel was analyzed. This data is provided for guidance purposes only.

13.4 Table 2 shows the fluorescence response of polycyclic aromatic and monoaromatic compounds using AccuStandard CRMs supplied in methanol. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2, using the same two calibrations in Table 1. Fluorescence response was calculated by dividing sample readings by the concentration of the standard used and shown as a percentage. Response varies depending on the size and shape of each molecule and which standard is used for calibration. In this case, the No. 2 diesel fuel standard fluoresces weaker (62%) compared to Sitelab's EDRO standard (100%) analyzed in Calibration 1. Sitelab's EDRO standard fluoresces stronger (162%) compared to No. 2 diesel fuel (100%) analyzed in Calibration 2. This difference is exhibited in the sample results. This data is provided for guidance purposes only.

13.5 Table 3 shows the fluorescence response of diesel range organics in a variety of fuels and oils exhibiting low to high DRO content. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2, using the same two calibrations in Tables 1 and 2. Samples consisted of AccuStandard CRMs, Non-Aqueous Phase Liquids (NAPL) collected from oil recovery wells from different sites, light crude oil using a Standard Reference Material (SRM) from National Institute of Standards & Technology (NIST) and other samples collected from retail stores or manufacturers for comparison. Heavy fuel oils, NAPLs, crude oil, coal tar and creosote samples were supplied in hexane with standards prepared in methanol for analysis. Gasolines, diesels, and other light-refined fuel oils were supplied in methanol with standards diluted further in methanol for analysis. Chemical Abstract Service (CAS) Registry Numbers for each source type is listed, where applicable. This data is provided for guidance purposes only.

13.6 Table 4 compares single laboratory accuracy and precision testing DRO in water using proficiency samples supplied by Environmental Resource Associates (ERA) and NSI Lab Solutions, LLC. Both vendors use ultra-low sulfur diesel fuel supplied in methanol for their products. Data performed using analyzer configuration specified in Sec. 6.2, with three calibrations performed using standards prepared in hexane. Water samples were spiked in clean tap water using 40 mL VOA vials and then extracted in hexane. Samples 1 were extracted 15 minutes after preparation; Samples 2 Duplicates were extracted 1 hour after preparation. The laboratory mean result and performance limits in ERA's and NSI's proficiency studies are shown for comparison. Percent recoveries (%R) in Calibrations 1 using the DRO standards provided by each vendor's product are close to 100% and are within the acceptance

limits. Percent recoveries in Calibration 2 and 3 were low, as expected, since ultra-low sulfur diesel fuels contain fewer aromatic hydrocarbons compared to No. 2 diesel fuel and Sitelab's EDRO standard. See References 3 and 4 in Sec. 16 for ERA and NSI certificates of analysis. This data is provided for guidance purposes only.

13.7 Table 5 compares single laboratory accuracy and precision testing DRO in soil using proficiency samples supplied by Environmental Resource Associates (ERA) and NSI Lab Solutions, LLC. Both vendors use ultra-low sulfur diesel fuel to prepare their soil samples, same source of fuel used to prepare their DRO standards for water analysis. Data performed using analyzer configuration specified in Sec. 6.2. with three calibrations performed using standards prepared in methanol. Samples 1 and Samples 2 Duplicates each contained 10-g of soil extracted in 20 mL methanol for 24 hours. The laboratory mean result and performance limits in ERA's and NSI's proficiency studies are shown for comparison. Percent recoveries (%R) in Calibrations 1 using the standards provided by each vendor's DRO in water product are close to 100% and are within the acceptance limits. Percent recoveries in Calibrations 2 and 3 were low, as expected, since low sulfur diesel fuels contain fewer aromatic hydrocarbons compared to No. 2 diesel fuel and the EDRO standard. See References 5 and 6 in Sec. 16 for ERA and NSI certificates of analysis. This data is provided for guidance purposes only.

13.8 Table 6 shows spike recovery analysis using a laboratory control sample performed by a single laboratory testing EDRO in soil samples spiked with NIST SRM 2779 Gulf of Mexico crude oil. Data performed using analyzer configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard in methanol. Samples consisted of clean sand, soil and clay collected from local sources and two lots of ERA CRM 570 TPH in Soil containing vacuum pump oil. Samples were spiked using a 10,000 ppm oil extract in hexane, same source used to prepare LCS standards in methanol for analysis to compare fluorescence response. Spiked and unspiked samples were analyzed using 5-g each extracted in 20 mL methanol for 24 hours. EDRO tests performed produced accurate recoveries >50%. The LCS standard fluoresces 1.33 times lower compared to EDRO due to the different composition of PAH compounds in the oil when analyzed in methanol. See Reference 7 in Sec. 16 for composition of polycyclic aromatic hydrocarbons in the oil. This data is provided for guidance purposes only.

13.9 Table 7 shows spike recovery and aqueous stability analysis using laboratory control sample performed by a single laboratory testing EDRO in fresh and salt water spiked with NIST SRM 2779 Gulf of Mexico crude oil. Data performed using analyzer configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard in hexane. Samples were spiked using a 10,000 ppm oil extract in methanol, same source used to prepare the LCS standard in hexane for analysis to compare fluorescence response. Spiked and unspiked samples were extracted in hexane and tested 30 minutes, 3 hours and 10 days after preparation. EDRO tests performed produced accurate recoveries >50%. Results demonstrate water samples are stable 10 days after preparation when spiked with the oil dissolved in methanol. The LCS standard fluoresces 1.5 times lower compared to EDRO due to the different composition of PAH compounds in the oil when analyzed in hexane. See Reference 7 in Sec. 16 for composition of polycyclic aromatic hydrocarbons in the oil. This data is provided for guidance purposes only.

13.10 Table 8 shows single laboratory precision for EDRO in soils testing blind U.S. EPA proficiency evaluation samples spiked with low concentrations of No. 2 diesel fuel. Data performed using analyzer configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard testing samples extracted in methanol. Split samples were analyzed by a certified laboratory using Method 8015M. The laboratory performed EDRO as the sum of the DRO and ORO concentrations in the samples. Samples were used to calculate the method detection limit

(MDL) in U.S. EPA's study. See Reference 1, Table 7-1, Sec. 16. This data is provided for guidance purposes only.

13.11 Table 9 compares EDRO results in soil performed in a multi-lab study testing split samples contaminated with crude oil from a pipeline spill in Nigeria. UVF data performed using two analyzers following configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard testing samples extracted in methanol. Samples were sent to two certified laboratories for confirmation analysis. Both laboratories performed Method 8015M testing samples extracted in methylene chloride. The Nigeria lab reported hydrocarbons in the C9 – C40 range; the U.S. lab reported hydrocarbons in the C10 – C36 range. EDRO results correlated well to each other and the two laboratory GC/FID results with relative percent difference (RPD) values <50%. This data is provided for guidance purposes only.

13.12 Table 10 shows EDRO results compared to Total EPH results using the Massachusetts Dept. of Environmental Protection (MADEP) Extractable Petroleum Hydrocarbon Method testing soils collected from a tank farm site contaminated with mixed fuel oils. Data performed by a single laboratory using analyzer configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard. Soils were analyzed on-site using 5-g each extracted in 10 mL methanol. Split samples having low to high concentrations were sent to a certified laboratory for analysis. Relative percent difference (RPD) values between the UVF EDRO and Total EPH were less than 50%. Total EPH was calculated as the sum of the two aliphatic fractions and the unadjusted aromatic fraction. MADEP's EPH Method is similar to Method 8015M; both detect diesel and oil range hydrocarbons using GC/FID. EPH is performed to meet specific regulatory cleanup limits in separate fractions. See Reference 8 in Sec. 16 for further guidance.

13.13 Table 11 shows EDRO results compared to Canada's Extractable Petroleum Hydrocarbons Method testing soils contaminated with heavy crude oil for disposal at landfill site. Data performed by a single laboratory using analyzer configuration specified in Sec. 6.2, calibrated to Sitelab's EDRO standard. Soils were analyzed using 5-g each extracted in 10 mL methanol. Split samples were sent to a certified laboratory for analysis. The EPH method detects hydrocarbons into separate ranges to meet specific regulatory cleanup limits. Relative percent difference (RPD) values between the UVF EDRO and sum of the F2 and F3 fractions were less than 50%. These fractions include the diesel and oil range hydrocarbons in the C10 – C34 range, similar to Method 8015M and MADEP Total EPH Method ranges. This data is provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

Field waste management procedures must also be consistent with Federal, State and local regulations.

16.0 REFERENCES

1. U.S. Environmental Protection Agency, Superfund Innovative Technology Evaluation Program, “Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil,” EPA Office of Research and Development, Publication No. EPA/600/R-01/080, September 2001.

2. North Carolina Department of Environmental Quality, Division of Waste Management, Underground Storage Tank Section, “Comprehensive Tables for Corrective Action Guidelines,” September 7, 2022.

3. Environmental Resource Associates, Certified Reference Material 764, “Diesel Range Organics (DRO) in Water,” Certificate of Analysis, Lot P315-764, June 29, 2021.

4. NSI Lab Solutions, LLC, Certified Reference Material QC-115, “Diesel in Water,” Certificate of Analysis, Lot U0223, April 18, 2022.

5. Environmental Resource Associates, Certified Reference Material 765, “Diesel Range Organics (DRO) in Soil,” Certificate of Analysis, Lot D115-765, November 5, 2021.

6. NSI Lab Solutions, LLC, Certified Reference Material SQC-115, “Diesel in Soil,” Certificate of Analysis, Lot U0223, December 5, 2022.

7. National Institute of Standards & Technology, Standard Reference Material 2779, “Gulf of Mexico Crude Oil,” Certificate of Analysis, March 2021.

8. Massachusetts Department of Environmental Protection, Office of Research and Standards, Bureau of Waste Site Cleanup, “Method for the Determination of Extractable Petroleum Hydrocarbons,” May 2004.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

FLUORESCENCE OF CERTIFIED REFERENCE MATERIALS USED TO ESTABLISH BASELINE CALIBRATIONS FOR DIESEL RANGE ORGANICS (DRO) ANALYSIS

UVF Analyzer with DRO Optics, Calibrations and Analysis in Methanol Solvent CRMs Containing High-Sulfur Diesel Fuel with CAS No. 68334-30-5, Tested at 10 ppm Concentrations	Voltage (RFU)	Calibration 1: No. 2 Diesel Fuel, AccuStandard FU-009-40X Response (PPM)	%D	Calibration 2: Sitelab EDRO Standard, (50% Weathered Diesel) CAL-042M Response (PPM)	%D
Sitelab EDRO Standard Response	9,532	16.2		10.0	
No. 2 Diesel Fuel Standard Response	5,942	10.0		6.2	
Response Factor Exhibited:	1.6x	1.6x		1.6x	
Other CRMs Suitable for DRO Calibrations:			%D		
No. 2 Diesel Fuel in DCM, AccuStandard FU-009-D-40X	6,060	10.2	102%	6.3	
No. 2 Diesel Fuel 100% (neat), AccuStandard FU-009N-1ML	6,220	10.4	104%	6.5	
No. 2 Diesel Fuel in Acetone, AccuStandard DRO-AK-102-LCS-10X-R1	5,503	9.2	92%	5.7	
Weathered Diesel CRMS by Same Manufacturer:					%D
50% Weathered No. 2 Diesel Fuel, AccuStandard FD2-W50-R1-10X	9,480	16.0		9.9	99%
75% Weathered No. 2 Diesel Fuel, AccuStandard FD2-W75-R1-10X	11,900	20.0		12.5	125%
Second Source Calibration Standards by Different Manufacturer:			%D		%D
Diesel Fuel #2 - 75% Weathered, Restek 31236	7,450	12.5		7.8	78%
Diesel Fuel #2 - Unweathered, Restek 31233	4,424	7.5	75%	4.7	
Response Factor Exhibited:	1.7x	1.7x		1.7x	

This data is provided for guidance purposes only. Fresh and weathered diesel fuel products made by different manufacturers were analyzed at 10 ppm and compared to AccuStandard's No 2. diesel fuel standard used to establish baseline DRO measurement and Sitelab's EDRO standard containing 50% weathered No. 2 diesel fuel.

CRMs shown meet the 1.5 to 2x response factor limit and percent difference (%D) values are within the 70 to 130% acceptance range. These products qualify as second source calibration standards suitable for this method. Raw fluorescence units (RFU) or voltage detected by the UVF is proportionate to sample concentration readings, which vary depending on which standard is used for calibration.

TABLE 2

FLUORESCENCE RESPONSE OF AROMATIC HYDROCARBONS COMPARING TWO CALIBRATIONS USED TO MEASURE DIESEL RANGE ORGANICS (DRO)

UVF Analyzer with DRO Optics, Calibrations and Analysis in Methanol Solvent	Molecular Weight ($g \cdot mol^{-1}$)	Carbon Number	Calibration 1: No. 2 Diesel Fuel, AccuStandard FU-009-40X Fluorescence Response (%)	Calibration 2: Sitelab EDRO, (50%W Diesel) CAL-042M Fluorescence Response (%)
Polycyclic Aromatic Compounds:				
Naphthalene	128	C10	134	84
2-Methylnaphthalene	142	C11	260	160
Phenanthrene	178	C14	1,460	900
Anthracene	178	C14	2,080	1,280
Benzo[a]Anthracene	228	C18	212	130
Chrysene	228	C18	1,200	740
Benzo[k]Fluoranthene	252	C20	376	230
Benzo[a]Pyrene	252	C20	200	122
Dibenz[a,h]Anthracene	278	C22	20	12
Sitelab EDRO Standard Response:			162	100
No. 2 Diesel Fuel Standard Response:			100	62
Monoaromatic Compounds:				
Benzene	78	C6	0.16	0.10
Toluene	92	C7	0.40	0.25
Ethylbenzene	106	C8	0.32	0.20
m-Xylene	106	C8	0.54	0.34
o-Xylene	106	C8	0.80	0.50
p-Xylene	106	C8	1.60	1.00
1,3,5-Trimethylbenzene	120	C9	2.30	1.50

This data is provided for guidance purposes only. Analytes provided in methanol using CRMs by AccuStandard. Fluorescence of individual compounds varies depending on the size and shape of each molecule and which standard is used for calibration. PAH compounds in the C10 – C20 range exhibit high response. Monoaromatic compounds in the C6 – C10 range exhibit very low response and contribute little to DRO detection in this method.

TABLE 3

FLUORESCENCE RESPONSE OF DIESEL RANGE ORGANICS IN FUELS AND OILS

UVF Analyzer with DRO Optics, Calibrations and Analysis in Methanol Solvent	CAS No.	Source	Calibration 1: No. 2 Diesel Fuel, AccuStandard FU-009-40X Fluorescence Response (%)	Calibration 2: Sitelab EDRO, (50%W Diesel) CAL-042M Fluorescence Response (%)
Automotive and Heating Fuels with Low to High DRO Content:				
Gasoline, Regular 87 Octane	8006-61-9	Retail	1.2	0.7
50% Weathered Gasoline	8006-61-9	CRM	10	6.0
Weathered Gasoline, UST Site	N/A	NAPL	16	10
Ultra-Low Sulfur Diesel Fuel	68476-34-6	CRM	12	7.5
Highway Diesel, Ultra-Low Sulfur	68476-34-6	Retail	29	18
No. 2 Fuel Oil	68476-30-2	CRM	110	68
Weathered Diesel, UST Site	N/A	NAPL	145	90
No. 4 Fuel Oil	68476-31-3	CRM	256	158
No. 6 Fuel Oil	68553-00-4	CRM	427	265
Other Fuels and Oils with Low to High DRO Content:				
Kerosene	8008-20-6	CRM	2.9	1.8
JET-A Jet Fuel	8008-20-6	CRM	8.0	5.0
Weathered Jet Fuel, UST Site	N/A	NAPL	16	10
Transformer Oil	64742-53-6	CRM	16	10
Light Crude Oil, NIST 2779	8002-05-9	SRM	122	75
Heat Transfer Fluid	101-84-8	Retail	240	150
Coal Tar, MGP Site	N/A	NAPL	640	400
Creosote, Wood Treatment Site	N/A	NAPL	1,200	750
Sitelab EDRO Standard Response:			162	100
No 2. Diesel Fuel Standard Response:			100	62

This data is provided for guidance purposes only. Response in fuels and oils varies in DRO content, shown here calibrated to AccuStandard's No 2. diesel fuel standard and Sitelab's EDRO standard containing 50% weathered No. 2 diesel fuel.

TABLE 4

DIESEL RANGE ORGANICS IN WATER TESTING ERA AND NSI PROFICIENCY SAMPLES

UVF Analyzer with DRO Optics Comparing 3 Calibrations, Samples Tested in Hexane	Sample 1 µg/L	Sample 2 Duplicate µg/L	Average Result µg/L	Certified Value µg/L	%R
PT Study 1: Environmental Resource Associates					
1. DRO Water Standard, ERA 764, Lot P315-764	1,798	1,714	1,756	1,770	99%
2. No. 2 Diesel Fuel Standard, AccuStandard FU-009-40X	368	350	359	1,770	20%
3. EDRO Calibration Standard, Sitelab CAL-042H	214	204	209	1,770	12%
ERA Proficiency Study, Lot P315-764 Diesel Range Organics Mean Result:			1,250	1,770	71%
QC Performance Acceptance Limits:			556 – 2,040		
PT Performance Acceptance Limits:			219 – 2,350		
PT Study 2: NSI Lab Solutions, LLC					
1. DRO Water Standard, NSI QC-115, Lot U0223	1,900	1,950	1,925	1,880	102%
2. No. 2 Diesel Fuel Standard, AccuStandard FU-009-40X	430	450	440	1,880	23%
3. EDRO Calibration Standard, Sitelab CAL-042H	270	280	275	1,880	15%
NSI Proficiency Study, Lot U0223 Diesel Range Organics Mean Result:			1,300	1,880	69%
PT Study Acceptance Limits:			415 – 2,460		

This data is provided for guidance purposes only. UVF performed using three calibrations using different standards available for comparison.

Samples spiked 1:1000 in tap water using DRO standards provided with each vendor's product. Samples extracted using hexane. Samples 1 were extracted 15 minutes after preparation. Samples 2 were extracted 1 hour after preparation.

DRO analysis performed best using ERA's and NSI's DRO standards. Percent recovery (%R) values are within each vendor's Acceptance Limits. Both ERA and NSI use ultra-low sulfur diesel (USLD), CAS #68476-34-6, in their water and soil proficiency testing products. Calibrations using Sitelab EDRO and AccuStandard No.2 Diesel Fuel produced lower recoveries due to their higher aromatic composition.

TABLE 5

DIESEL RANGE ORGANICS IN SOIL TESTING ERA AND NSI PROFICIENCY SAMPLES

UVF Analyzer with DRO Optics Comparing 3 Calibrations, Samples Tested in Methanol	Sample 1 mg/Kg	Sample 2 Duplicate mg/Kg	Average Result mg/Kg	Certified Value mg/Kg	%R
PT Study 1: Environmental Resource Associates					
1. DRO Water Standard, ERA 764, Lot P315-764	2,010	1,710	1,860	1,850	101%
2. No. 2 Diesel Fuel Standard, AccuStandard FU-009-40X	340	290	315	1,850	17%
3. EDRO Calibration Standard, Sitelab CAL-042M	210	180	195	1,850	11%
	ERA Proficiency Study, Lot D115-765				
	Diesel Range Organics Mean Result:		1,350	1,850	73%
	QC Performance Acceptance Limits:		829 – 2,150		
	PT Performance Acceptance Limits:		478 – 2,220		
PT Study 2: NSI Lab Solutions, LLC					
1. DRO Water Standard, NSI QC-115, Lot U0223	2,040	2,216	2,128	2,200	97%
2. No. 2 Diesel Fuel Standard, AccuStandard FU-009-40X	484	522	503	2,200	23%
3. EDRO Calibration Standard, Sitelab CAL-042M	300	326	313	2,200	14%
	NSI Proficiency Study, Lot U0223				
	Diesel Range Organics Mean Result:		2,114	2,200	96%
	PT Study Acceptance Limits:		793 – 3,610		

This data is provided for guidance purposes only. UVF performed using three calibrations using different standards available for comparison.

Soils provided by each vendor were analyzed in duplicate using 10 grams each extracted in 20 mL methanol for 24 hours.

DRO analysis performed best using ERA's and NSI's DRO standards. Percent recovery (%R) values are within each vendor's Acceptance Limits. Both ERA and NSI use ultra-low sulfur diesel (USLD), CAS #68476-34-6, in their water and soil proficiency testing products. Calibrations using Sitelab EDRO and AccuStandard No.2 Diesel Fuel produced lower recoveries due to their higher aromatic composition.

TABLE 6

SPIKE RECOVERY USING LABORATORY CONTROL SAMPLE TESTING EDRO IN SOILS SPIKED WITH NIST SRM 2779 GULF OF MEXICO CRUDE OIL

UVF Calibrated to EDRO using Sitelab CAL-042M, Samples Tested in Methanol	Sample with No Spike mg/Kg	Sample with 100 ppm Spike mg/Kg	LCS Oil Standard 100 ppm Response mg/Kg	%R
Beach Sand	0.5	73	75	97%
Sandy Loam Soil	0.7	70	75	92%
Clay	0.3	65	75	86%
ERA 570 TPH Soil 1	33	99	75	88%
ERA 570 TPH Soil 2	57	116	75	77%

This data is provided for guidance purposes only. EDRO tests performed exhibited percent recoveries (%R) >50%.

Environmental Resource Associates (ERA) 570 TPH Soil CRMs contain vacuum pump oil with different composition.
TPH in Soil 1, Lot D118-632, contains 579 mg/Kg TPH by Gravimetric and 712 mg/Kg TPH by Infrared.
TPH in Soil 2, Lot D116-632, contains 1,770 mg/Kg TPH by Gravimetric and 2,180 mg/Kg by Infrared.

TABLE 7

SPIKE RECOVERY AND AQUEOUS STABILITY USING LABORATORY CONTROL SAMPLE TESTING EDRO IN WATER SPIKED WITH NIST SRM 2779 GULF OF MEXICO CRUDE OIL

UVF Calibrated to EDRO using Sitelab CAL-042H, Samples Tested in Hexane		Sample with No Spike mg/L	Sample with 10 ppm Spike mg/L	LCS Oil Standard 10 ppm Response mg/L	%R
Samples Extracted Same Day and 10 Days After Preparation					
30 Minutes	Fresh Water	0.0	6.8	6.6	103%
	Salt Water	0.0	6.2	6.6	94%
3 Hours	Fresh Water	0.0	6.0	6.6	91%
	Salt Water	0.0	6.7	6.6	102%
10 Days	Fresh Water	0.0	5.7	6.6	86%
	Salt Water	0.0	6.2	6.6	94%

This data is provided for guidance purposes only. EDRO tests performed exhibited percent recoveries (%R) >50%.

TABLE 8

EXTENDED DIESEL RANGE ORGANICS IN SOILS TESTING BLIND U.S. EPA PROFICIENCY EVALUATION SAMPLES SPIKED WITH LOW CONCENTRATIONS OF NO. 2 DIESEL FUEL

Contaminant, Matrix	U.S. EPA Sample ID Number	Certified Value mg/Kg	UVF EDRO Result mg/Kg	Lab 8015M EDRO Result mg/Kg	Acceptance Limits mg/Kg
No. 2 Diesel Fuel, Spiked in 7 Soils used for MDL Study	PE S66	37.3	17.9	12.0	18.1 – 47.4
	PE S67	37.3	18.9	16.5	18.1 – 47.4
	PE S68	37.3	17.5	13.7	18.1 – 47.4
	PE S69	37.3	15.8	16.4	18.1 – 47.4
	PE S70	37.3	18.1	17.4	18.1 – 47.4
	PE S71	37.3	19.0	17.2	18.1 – 47.4
	PE S72	37.3	18.5	14.8	18.1 – 47.4
Method Detection Limit (MDL) Reported:			3.4	6.32	

This data is provided for guidance purposes only. Data taken from Table 7.1 in Reference 1, Sec. 16.

TABLE 9

EDRO RESULTS COMPARED TO TWO CERTIFIED LABORATORY RESULTS USING EPA METHOD 8015M TESTING SOILS WITH HIGH CONCENTRATIONS OF NIGERIA CRUDE OIL

Split Samples Collected from Pipeline Spill Site	Sample 1 mg/Kg	Sample 2 mg/Kg
UVF EDRO Results: Field Sample, Nigeria	7,160	15,150
EPA Method 8105M Results: Nigeria Certified Laboratory	6,829	14,999
RPD:	5%	1.0%
UVF EDRO Results: Confirmatory Sample, United States	7,800	15,430
EPA Method 8015M Results: United States Certified Laboratory	10,200	24,800
RPD:	27%	47%

This data is provided for guidance purposes only. UVF performed using configuration in Sec. 6.2., calibrated to Sitelab's EDRO standard testing soils with methanol. Nigeria lab performed EPA Method 8015M by GC/FID, detecting hydrocarbons in the C9 – C40 range. U.S. lab performed EPA Method 8015M by GC/FID, detecting hydrocarbons in the C10 – C36 range. Relative percent difference (RPD) values were <50% comparing EDRO and GC/FID results.

TABLE 10

EDRO RESULTS COMPARED TO TOTAL EPH RESULTS USING MADEP EXTRACTABLE PETROLEUM HYDROCARBONS METHOD TESTING SOILS FROM FUEL OIL SITE

Soils Collected from Mixed Fuel Oil Site	Lab EPH C9-C18 Aliphatics mg/Kg	Lab EPH C19-C36 Aliphatics mg/Kg	Lab EPH C11-C22 Aromatics mg/Kg	Total EPH Result mg/Kg	UVF EDRO Result mg/Kg	RPD
1	67	78	98	243	350	36%
2	270	57	140	487	390	22%
3	1,600	170	700	2,470	1,530	47%
4	1700	150	680	2,530	2,200	14%
5	2,700	220	1,200	4,120	4,400	7%
6	3,600	290	1,800	5,690	6,000	5%
7	8,800	750	2,600	12,150	11,200	8%
8	12,000	1,100	3,600	16,700	14,400	15%

This data is provided for guidance purposes only. UVF performed using configuration in Sec. 6.2., calibrated to Sitelab's EDRO standard testing soils with methanol. Laboratory performed MADEP EPH Method by GC/FID. Total EPH calculated as the sum of aliphatic and aromatic fractions. Relative percent difference (RPD) values exhibited in example results were <50%.

TABLE 11

EDRO RESULTS COMPARED TO EPH RESULTS USING CANADA EXTRACTABLE PETROLEUM HYDROCARBONS METHOD TESTING SOILS WITH HEAVY CRUDE OIL

Soils from Landfill Site with Crude Oil	Lab EPH C10-C16 F2 Fraction mg/Kg	Lab EPH C16-C34 F3 Fraction mg/Kg	Lab F2 + F3 C10-C34 EPH Fractions mg/Kg	UVF EDRO Result mg/Kg	RPD
1	153	2,280	2,433	2,245	8%
2	216	2,300	2,516	2,392	5%
3	302	2,580	2,882	2,429	17%
4	236	2,640	2,876	2,594	10%
5	303	3,560	3,560	3,374	5%

This data is provided for guidance purposes only. UVF performed using configuration in Sec. 6.2., calibrated to Sitelab's EDRO standard testing soils with methanol. Laboratory performed Canada EPH Method by GC/FID. The F2 and F3 fractions were added together to report diesel and oil range hydrocarbons, similar to EDRO's carbon range sensitivity. Relative percent difference (RPD) values exhibited in example results were <50%.

FIGURE 1

2017 NORTH CAROLINA DEPARTMENT OF ENVIRONMENTAL QUALITY REGULATORY GUIDELINES USING UVF AND GAS CHROMATOGRAPHY ANALYTICAL METHODS

Table 3
Approved Methods for Soil Analyses at Petroleum UST Closures and Over-Excavation and at Site Checks

Suspected Contaminant	Analytical Methods for Tank Closure, Site Check, or Other Preliminary Investigation Samples	Analytical Methods for Samples from an Over-Excavation Following a Release Abatement
1a. Low Boiling Point Fuels: *(gasoline, gasohol, aviation gasoline, etc.)*[a]	MADEP VPH – GRO Range[b] **or** EPA 8260B – GRO Range[b] **or** EPA 8015C TPH-GRO[b] **or** UVF-TPH (GRO)[b,c]	EPA 8260B **and** MADEP VPH
1b. Ethanol-Gasoline Blends *(of E85 and greater)*	EPA 8260B *(w/ Ethanol, ETBE, TAA, TAME, TBA, & TBF)*	EPA 8260B *(w/ Ethanol, ETBE, TAA, TAME, TBA, & TBF)* **and** MADEP VPH
2. Medium/High Boiling Point Fuels: *(kerosene, diesel, jet fuels, fuel oil #2, biodiesel containing diesel, Varsol, mineral spirits, naphtha, etc.)*	MADEP VPH – GRO Range[b] **or** EPA 8260B – GRO Range[b] **or** EPA 8015C TPH-GRO[b] **or** UVF-TPH (GRO)[b,c] **and** EPA 8015C TPH-DRO **or** UVF for TPH (DRO)[c]	EPA 8260B, EPA 8270D, MADEP VPH, **and** MADEP EPH
3. Heavy Fuels: *(#4, #5, #6 fuel oils, motor oil, hydraulic fluid, Mineral oil*[d]*, etc.)*	EPA 8015C for TPH-DRO **or** UVF for TPH (DRO)[c]	EPA 8270D **and** MADEP EPH
4. Used / Waste Oil[e]	EPA 8260B, EPA 8270D, MADEP VPH, MADEP EPH, (**or** UVF for TPH and PAH)[c] **and** EPA 3050B or 3051A Prep: Total Metals (Cr & Pb),	EPA 8260B, EPA 8270D, MADEP VPH, MADEP EPH, **and** EPA 3050B or 3051A Prep: Total Metals (Cr and Pb),

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a For tanks in operation prior to 1996 with a potential for storage of leaded fuel, or tanks used to store aviation gasoline or leaded racing gasoline at any point, analyze for Pb, EPA 3050B or 3051A Prep: Total Metals (Pb).

b During DEQ evaluation of alternate TPH Action Limits, also analyze and report individual benzene, ethylbenzene, toluene, and xylenes (o-, m-, & p-; mixed) using EPA 8260, EPA 8021, or MADEP VPH.

c Only UVF technology with product (fuel) identification and calibration approved by DWM is allowed as a TPH equivalent. (Other equivalent methods for TPH analysis may be approved by DWM for the initial investigation if determined to meet these requirements.)

d Carbon chains in mineral oils range from approximately C_{12}-C_{45}.

e For any waste oil investigations other than at a service station or garage, also sample for pesticides using EPA 8081B and polychlorinated biphenyl (PCBs) using EPA 8082A