METHOD 8660

TOTAL PETROLEUM 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 Total Petroleum hydrocarbons (TPH) using the source oil or fuel for calibration and analysis. Specifically, this method detects aromatic hydrocarbons in oils, fuels and other petrogenic or pyrogenic products. This method is intended for screening purposes.

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, TPH contaminated samples contain many aromatic compounds which co-fluoresce with UVF instrumentation. If analyzing individual analytes is required, refer to Method 8000 for guidance.

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

1.4 This method differs from Method 8650 for TPH GRO + DRO, where gasoline range and diesel range hydrocarbons are analyzed separately by UVF and results are added together to report TPH.

1.5 Source oils vary considerably and include a large number of refined petroleum products (e.g. gasolines, diesel fuels) and unrefined petroleum products (e.g. crude oils, heavy fuel oils). This method was developed using National Institute of Standards & Technology (NIST), Standard Reference Material (SRM) 2779 Gulf of Mexico crude oil. This oil fluoresces well using a variety of different UV lights, optical configurations and solvents. Refer to the method performance tables in Sec. 13. NIST SRM 2779 oil extracted in hexane fluoresces stronger compared to the oil extracted in methanol. Oil extracts analyzed by a laboratory using GC/FID instrumentation in Figures 1 and 2 show chromatograms and hydrocarbon content detected comparing the two solvents. See Reference 1 in Sec. 16 for composition of polycyclic aromatic hydrocarbons in the oil.

1.6 Choosing the appropriate calibration standard is dependent on the type or age of petroleum in a sample from each site. Results may be biased low or biased high if the wrong standard is selected for calibration and analysis. If Non-Aqueous Phase Liquids (NAPL) are available on a site, use the NAPL collected from each well for calibration and analysis. NAPLs often contain weathered, degraded or commingled contaminants and will fluoresce differently compared to fresh fuel or oil releases. If the source oil is not available or is unknown, use Method 8650 for analysis.

1.7 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 product or refer to Method 3500 for alternative sample preparation methods.

2.2 Hydrocarbons in samples can be measured using UVF instruments fitted with appropriate excitation and emission optical filters and ultraviolet light sources. This method is site-specific, since sensitivity varies depending on the types and quantities of aromatic hydrocarbons in the source oil or fuel used for calibration and analysis.

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 configurations 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.

6.2.1 Configuration for crude oils and heavy fuel oils: Use a near UV light source in the 365-nm to 375-nm range, fitted with narrow band excitation filters in the 360-nm to 380-nm range and broad band emission filters in the 410-nm to 600-nm range. In general, these configurations are sensitive to polycyclic aromatic hydrocarbons in the C14 to C50 carbon range.

6.2.2 Configuration for refined fuel oils: Use a deep UV light source in the 254-nm to 280-nm range, fitted with narrow band excitation filters in the 254-nm to 280-nm range and broad band emission filters in the 300-nm to 400-nm range. In general, these configurations are sensitive to polycyclic aromatic hydrocarbons in the C10 to C40 carbon range. Configurations specified in Method 8640 for diesel range organics may be used.

6.2.3 Configuration for light-refined fuel oils: Use a deep UV 254-nm or 255-nm light source, fitted with a 254-nm narrow band excitation filter and a 280-nm narrow band emission filter. This configuration is specified in Method 8630 for gasoline range organics and is sensitive to monoaromatic hydrocarbons in the C6 to C10 carbon range. This configuration is most suitable for source oils or fuels high in volatile aromatic composition, including benzene, toluene, ethylbenzene, and xylenes (BTEX).

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. Prepare standards using the source oil extracted and diluted in the appropriate solvents at concentrations suitable for analysis. Calibration standards should be replaced if comparison with check standards indicates a problem. See Method 8000 for

additional information on the preparation of calibration standards. Consult with the UVF manufacturer for further guidance and if alternative TPH standards are available 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 the fluorescence response of aromatic hydrocarbons, fuels and oils comparing three UVF analyzers fitted with different UV light and optical filters calibrated to a light crude oil. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1 and 6.2.2. Crude oil calibrations performed using NIST SRM 2779, extracted in hexane with calibration standards prepared in methanol for analysis. Fluorescence response was calculated by dividing sample readings by the concentration of the standard used and shown as a percentage. Samples consisted of AccuStandard Certified Reference Materials (CRMs), gasoline and diesel fuel collected from local gas stations and three crude oils having different API gravity. Chemical Abstract Service (CAS) Registry Numbers for each sample type is listed. No. 6 and No. 4 fuel oils and crude oils were supplied in hexane with standards prepared in methanol for analysis. Aromatic compounds, gasoline, diesel fuels and No. 2 fuel oil were supplied in methanol with standards diluted further in methanol for analysis. Fluorescence varies depending on the size and shape of aromatic molecules and composition of hydrocarbons in different petroleum products. Fluorescence also varies depending on which instrument configuration is used for analysis. In this case, NIST SRM 2779 fluoresces well using all three UVF analyzers and is suitable to validate this method. This data is provided for guidance purposes only.

13.4 Table 2 shows fluorescence comparing NIST SRM 2779 crude oil extracts and standards prepared in hexane and methanol. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1, calibrated using Sitelab Corporation p/n CAL-057H in hexane and p/n CAL-057M in methanol used to factory calibrate Sitelab's UVF-Trilogy analyzer. Raw Fluorescence Units (RFU) response is voltage detected by the analyzer with or without calibration and is proportionate to sample concentration response when measured using Calibration 1 and Calibration 2. Relative percent difference (RPD) values are similar. Fluorescence varies depending on which solvents are used to extract the oil and prepare

standards for analysis. Oil samples were extracted for 24 hours at 10,000 ppm using the two solvents, which exhibit different extraction efficiency. Methanol does not extract asphaltenes in the oil; they do not dissolve and stick inside the glass extraction vial, producing weaker fluorescence response. Hexane dissolves all the asphaltene content into solution, producing stronger fluorescence response. This is consistent with concentration and chromatogram differences in Figures 1 and 2. This data is provided for guidance purposes only.

13.5 Table 3 shows spike recovery analysis comparing three UVF analyzers testing clean soils spiked with NIST SRM 2779 crude oil. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1 and 6.2.2, using three UVF analyzers calibrated using the oil extracted in hexane with standards prepared in methanol for analysis. Samples consisted of beach sand, sandy loam soil and clay collected from local sources. Samples 1 and 2 prepared using 10-g and 5-g aliquots, respectively, extracted in 20 mL methanol for 24 hours. Low Spikes prepared using a 10,000 ppm oil extract dissolved in hexane. High Spikes prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added and were >50% in most of the results. Lower recoveries observed in the low spiked clay samples using Analyzers 2 and 3 are due to matrix effects. Clay absorbs hydrocarbons and prohibits extraction at these wavelengths.

13.6 Table 4 shows spike recovery analysis comparing three UVF analyzers testing contaminated soils spiked with NIST SRM 2779 crude oil. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1 and 6.2.2, using three UVF analyzers calibrated to the oil extracted in hexane with standards prepared in methanol and factory calibrations using Sitelab calibration products listed for comparison. Samples consisted of two lots of Environmental Resource Associates (ERA) CRM 570 TPH in Soil, used to validate gravimetric and infrared test methods. ERA uses vacuum pump oil in this product which dissolves poorly in methanol and is low in aromatic content. Samples prepared using 10-g soil extracted in 20 mL methanol for 24 hours. Spiked samples prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added and were >50% in most of the results using the crude oil calibrations. Results vary compared to the factory calibrations due to the different composition of aromatic hydrocarbons in the oil compared to the Sitelab standards. See Reference 2 and 3 in Sec. 16 for ERA 570 certificates of analysis. This data is provided for guidance purposes only.

13.7 Table 5 shows spike recovery analysis comparing three UVF analyzers testing water spiked with NIST SRM 2779 crude oil. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1 and 6.2.2, calibrated using a 10,000 ppm oil extract in methanol with calibration standards prepared in hexane and factory calibrations using Sitelab calibration products listed for comparison. Samples prepared in triplicate by spiking aliquots of the oil extracted in methanol at two concentrations using clean fresh water and salt water collected from local sources. Samples were extracted and analyzed the same day and 10 days after preparation to check aqueous stability. Percent recoveries (%R) values were >80% in most of the results using the crude oil calibrations. Results vary compared to the factory calibrations due to the different composition of aromatic hydrocarbons in the oil compared to the Sitelab standards. Recoveries in the 10-day old samples were lower due to sample degradation over time. This data is provided for guidance purposes only.

13.8 Table 6 shows aqueous stability analysis comparing three UVF analyzers testing water spiked with NIST SRM 2779 crude oil without solvent extraction. Data performed by a single laboratory with analyzer configurations specified in Sec. 6.2.1 and 6.2.2, calibrated using a 10,000 ppm oil extract in methanol with calibration standards prepared in hexane for analysis. Samples prepared by spiking aliquots of the oil extracted in methanol at two concentrations

using clean salt water and fresh water collected from local sources. Unspiked water samples were analyzed and are shown for comparison. Samples spiked in salt water are more stable over time; the percent drop in concentration from 5 minutes to 10 days was lower compared to fresh water spiked samples. Additionally, analyzers 2 and 3 exhibited higher readings in the samples compared to the spiked concentrations. Analyzer 1 exhibited lower readings compared to the spiked concentrations. This is due to the UV light and optical filters used and differences in the oil's solubility in the water at these wavelengths. In this study, samples were tested over time without solvent extraction to check sample degradation and to mimic fluorescence-based oil in water (OIW) monitors used to detect hydrocarbons in water continuously using flow cells, submersible probes or sensors. OIW monitors are calibrated to spiked water solutions using the source oil and the unspiked source water is used for the blank. As demonstrated here, spiked water samples used by OIW monitors to calibrate would perform best soon after preparation. 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. National Institute of Standards & Technology, Standard Reference Material 2779, "Gulf of Mexico Crude Oil," Certificate of Analysis, March 2021.

2. Environmental Resource Associates, Certified Reference Material 570, “Total Petroleum Hydrocarbons (TPH) in Soil,” Certificate of Analysis, Lot D116-632, January 26, 2022.

3. Environmental Resource Associates, Certified Reference Material 570, “Total Petroleum Hydrocarbons (TPH) in Soil,” Certificate of Analysis, Lot D118-632, July 27, 2022.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

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

TABLE 1

FLUORESCENCE RESPONSE OF AROMATIC HYDROCARBONS, FUELS AND OILS COMPARING THREE UVF ANALYZERS CALIBRATED TO LIGHT CRUDE OIL

NIST SRM 2779 Crude Oil Calibrations and Analysis in Methanol Solvent	CAS No.	UVF-Trilogy: 255-nm UV, EDRO Optics Fluorescence Response (%)	UVF-Trilogy: 365-nm UV, TPHOIL Optics Fluorescence Response (%)	UVF-500D, 375-nm UV, Channel A Optics Fluorescence Response (%)
Aromatic Compounds and Carbon Size:				
Benzene, C6	71-43-2	0.1	0.0	0.0
m-Xylene, C8	108-38-3	0.3	0.0	0.0
Naphthalene, C10	91-20-3	112	0.1	0.1
Phenanthrene, C14	85-01-8	1,200	11	13
Anthracene, C14	120-12-7	1,730	1,700	2,000
Benzo[a]Anthracene, C18	56-55-3	172	350	120
Chrysene, C18	218-01-9	970	4.8	3.0
Benzo[a]Pyrene, C20	50-32-8	160	13,000	12,500
Dibenz[a,h]Anthracene, C22	53-70-3	15	55	47
Automotive Fuels, Heating Oils and Crude Oils:				
Gasoline, Regular 87 Octane	8006-61-9	1.0	0.1	0.1
Highway Diesel, Ultra Low Sulfur	68476-34-6	24	0.6	0.5
No. 2 Diesel Fuel	68334-30-5	83	2.8	2.1
No. 2 Fuel Oil	68476-30-2	90	3.5	3.4
No. 4 Fuel Oil	68476-31-3	206	200	200
No. 6 Fuel Oil	68553-00-4	350	420	440
Crude Oil, API Gravity 40°	8002-05-9	42	45	48
Crude Oil, API Gravity 32°	8002-05-9	224	275	280
Crude Oil, API Gravity 20°	8002-05-9	97	125	130
NIST SRM 2779 Oil Calibration Standard Response:		100	100	100

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation comparing three UVF analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in hexane with standards prepared in methanol. Fluorescence varies depending on the size and shape of aromatic molecules and composition of hydrocarbons in different petroleum products.

TABLE 2

FLUORESCENCE OF LIGHT CRUDE OIL EXTRACTS AND STANDARDS USING HEXANE AND METHANOL SOLVENTS COMPARED TO UVF TPH FACTORY CALIBRATIONS

			UVF-Trilogy, 365-nm UV with TPHOIL Optics:		
NIST SRM 2779 Crude Oil Extracts, Solvent Used	Standard Concentration, Solvent Used		Voltage, Raw Fluorescence Units (RFU)	Calibration 1, Sitelab CAL-057H mg/L	Calibration 2, Sitelab CAL-057M mg/Kg
10,000 ppm Oil Extract in Hexane Solvent	10 ppm Hexane Standard		14,600	18.8	21.0
	10 ppm Methanol Standard		13,170	16.9	18.6
		RPD:	10%	11%	12%
10,000 ppm Oil Extract in Methanol Solvent	10 ppm Hexane Standard		5,280	7.0	7.8
	10 ppm Methanol Standard		6,640	8.9	9.9
		RPD:	23%	24%	23%
Factory Calibration Standard and Solvent Blank Response:					
Sitelab CAL-057H	10 ppm Hexane Standard		7,550	10.0	11.0
Sitelab CAL-057M	10 ppm Methanol Standard		6,780	9.0	10.0
		RPD:	11%	11%	10%
	Hexane Solvent Blank		80	0.0	0.0
	Methanol Solvent Blank		90	0.0	0.0

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using analyzer sensitive to crude oils. Oil standards made from NIST SRM 2779 Gulf of Mexico light crude oil and were measured to two factory calibrations using standards in hexane and methanol made from a different source of hydrocarbons.

Raw Fluorescence Units (RFU) response is voltage detected by the analyzer with or without calibration and is proportionate to sample concentration readings; relative percent difference (RPD) values are similar.

Fluorescence varies depending on which solvents are used to extract the oil and prepare standards for analysis. Oils were extracted for 24 hours using methanol and hexane. The solvents exhibit different extraction efficiency. Methanol does not extract asphaltenes in the oil; they do not dissolve and stick inside the glass extraction vial. Hexane dissolves all the asphaltene content into solution.

TABLE 3

SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS
TESTING CLEAN SOILS SPIKED WITH NIST SRM 2779 CRUDE OIL

Analyzers Calibrated to NIST 2779, Samples Tested in Duplicate	Sample with No Spike mg/Kg	Low Spike 100 ppm mg/Kg	%R	High Spike 5,000 ppm mg/Kg	%R
1. UVF-Trilogy, 255-nm UV with EDRO Optics:					
Beach Sand 1	0.7	96	95%	4,420	88%
Beach Sand 2	0.6	95	94%	4,560	91%
Sandy Loam 1	1.1	92	91%	4,130	83%
Sandy Loam 2	1.1	92	91%	4,540	91%
Clay 1	0.5	84	84%	4,000	80%
Clay 2	0.4	87	87%	4,530	91%
2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:					
Beach Sand 1	3.2	87	83%	3,400	68%
Beach Sand 2	2.8	88	85%	3,710	74%
Sandy Loam 1	6.0	58	52%	2,700	54%
Sandy Loam 2	6.3	65	59%	3,510	70%
Clay 1	0.6	32	32%	2,500	50%
Clay 2	0.7	35	34%	3,370	67%
3. UVF-500D, 375-nm UV with Channel A Optics:					
Beach Sand 1	14.6	105	90%	3,520	70%
Beach Sand 2	16.4	113	96%	3,765	75%
Sandy Loam 1	9.2	66	57%	2,800	56%
Sandy Loam 2	9.6	74	65%	3,230	64%
Clay 1	1.2	35	34%	2,600	52%
Clay 2	1.0	38	37%	3,155	63%

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters calibrated to NIST SRM 2779 using crude oil extracted in hexane with standards prepared in methanol.

Samples 1 and 2 prepared using 10-g and 5-g aliquots extracted in 20 mL methanol solvent for 24 hours. Low Spikes prepared using a 10,000 ppm oil extract dissolved in hexane. High Spikes prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added.

TABLE 4

SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS
TESTING CONTAMINATED SOILS SPIKED WITH NIST SRM 2779 CRUDE OIL

UVF Analyzers and Calibrations Performed	ERA 570 TPH in Soil CRMs	Sample with No Spike mg/Kg	Sample with Spike mg/Kg	Oil Spike Concentration mg/Kg	%R
1. UVF-Trilogy, 255-nm UV with EDRO Optics:					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	76	3,900	5,000	76%
	Soil Lot 2	45	4,590	5,000	91%
Factory Calibration, CAL-042M	Soil Lot 1	57	3,000	5,000	59%
	Soil Lot 2	33	3,510	5,000	70%
2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	121	2,500	5,000	48%
	Soil Lot 2	120	3,100	5,000	60%
Factory Calibration, CAL-057M	Soil Lot 1	236	4,850	5,000	92%
	Soil Lot 2	233	5,780	5,000	116%
3. UVF-500D, 375-nm UV with Channel A Optics:					
Crude Oil Calibration, NIST SRM 2779	Soil Lot 1	152	2,560	5,000	48%
	Soil Lot 2	175	3,325	5,000	63%
Factory Calibration, CAL-056M-500D	Soil Lot 1	308	5,120	5,000	96%
	Soil Lot 2	350	6,650	5,000	126%
ERA 570 TPH Concentrations:	Soil Lot 1, D116-632	1,770 mg/Kg by Gravimetric 2,180 mg/Kg by IR			
	Soil Lot 2, D118-632	579 mg/Kg by Gravimetric 712 mg/Kg by IR			

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in hexane with standards prepared in methanol. Factory calibrations performed using Sitelab calibration products listed for comparison.

Samples prepared using 10-g soil extracted in 20 mL methanol solvent for 24 hours. Spiked samples prepared using the oil. Percent recovery (%R) values account for concentrations in samples with no spike added.

Environmental Resource Associates (ERA) 570 TPH in Soil Certified Reference Material (CRM) analyzed using two lots with different composition. ERA uses vacuum pump oil in this product which dissolves poorly in methanol and is low in aromatic content, detected here with no spike added.

TABLE 5

SPIKE RECOVERY ANALYSIS COMPARING THREE UVF ANALYZERS
TESTING FRESH AND SALT WATER SPIKED WITH NIST SRM 2779 CRUDE OIL

UVF Analyzers and Calibrations Performed		10 ppm Spiked Samples		20 ppm Spiked Samples	
		Fresh Water	Salt Water	Fresh Water	Salt Water
Samples Extracted Same Day and 10 Days After Preparation		Recovery %	Recovery %	Recovery %	Recovery %
1. UVF-Trilogy, 255-nm UV with EDRO Optics:					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	101	95	88	89
	3 Hours	92	100	83	91
	10 Days	86	93	82	84
Factory Calibration, CAL-042H	30 Minutes	68	62	59	59
	3 Hours	60	67	54	61
	10 Days	57	62	55	56
2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	100	94	92	95
	3 Hours	88	101	83	99
	10 Days	80	86	82	81
Factory Calibration, CAL-057H	30 Minutes	71	67	65	68
	3 Hours	63	72	59	70
	10 Days	57	61	58	58
3. UVF-500D, 375-nm UV with Channel A Optics:					
Crude Oil Calibration, NIST SRM 2779	30 Minutes	94	90	86	89
	3 Hours	81	96	76	97
	10 Days	78	81	80	77
Factory Calibration, CAL-056H-500D	30 Minutes	52	50	48	49
	3 Hours	45	53	42	54
	10 Days	43	45	44	43

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 extracted in methanol with standards prepared in hexane. Factory calibrations performed using Sitelab calibration products listed for comparison.

TABLE 6

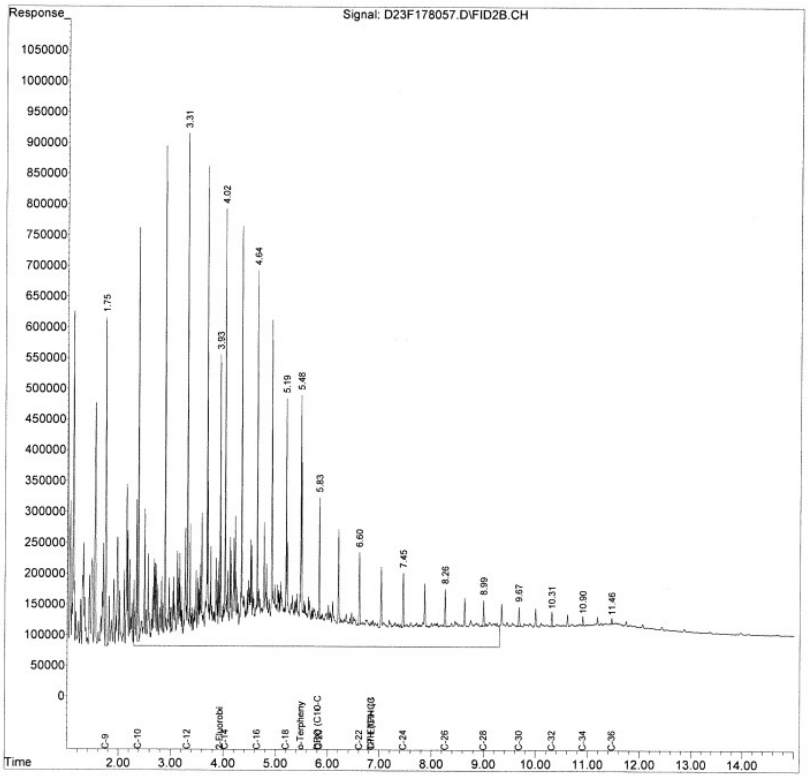
AQUEOUS STABILITY ANALYSIS COMPARING THREE UVF ANALYZERS TESTING WATER SPIKED WITH NIST SRM 2779 CRUDE OIL WITHOUT SOLVENT EXTRACTION

Analyzers Calibrated to NIST 2779 Crude Oil, Samples Tested Without Solvent Extraction Over Time	5 Min. mg/L	30 Min. mg/L	1 Hour mg/L	4 Hours mg/L	24 Hours mg/L	5 Days mg/L	10 Days mg/L	%Drop in Conc.
1. UVF-Trilogy, 255-nm UV with EDRO Optics:								
10 ppm Salt Water Spike	4.4	4.3	4.2	4.1	3.9	3.7	3.4	23%
20 ppm Salt Water Spike	7.2	7.0	6.8	6.6	5.9	5.6	5.2	28%
10 ppm Fresh Water Spike	5.9	5.8	5.8	5.6	4.4	3.6	3.4	42%
20 ppm Fresh Water Spike	9.5	9.3	9.3	8.8	6.2	5.1	5.0	47%
Salt Water, No Spike Added	0.0							
Fresh Water, No Spike Added	0.0							
2. UVF-Trilogy, 365-nm UV with TPHOIL Optics:								
10 ppm Salt Water Spike	17.5	17.1	16.6	16.7	15.0	14.0	12.4	29%
20 ppm Salt Water Spike	34.3	33.4	33.3	36.0	27.6	25.0	22.0	36%
10 ppm Fresh Water Spike	15.9	15.5	15.4	16.7	15.1	8.1	6.2	61%
20 ppm Fresh Water Spike	30.0	30.5	30.6	33.2	26.9	13.1	11.8	61%
Salt Water, No Spike Added	1.8							
Fresh Water, No Spike Added	0.7							
2. UVF-500D, 375-nm UV with Channel A Optics:								
10 ppm Salt Water Spike	16.8	16.1	15.9	16.4	14.1	13.5	12.4	26%
20 ppm Salt Water Spike	30.7	30.4	30.4	32.4	25.0	23.0	22.0	28%
10 ppm Fresh Water Spike	14.5	14.3	14.3	15.3	14.2	8.1	6.0	59%
20 ppm Fresh Water Spike	27.1	26.8	27.1	29.4	24.7	13.4	11.7	57%
Salt Water, No Spike Added	2.6							
Fresh Water, No Spike Added	1.6							

This data is provided for guidance purposes only. UVF performed by Sitelab Corporation using three analyzers fitted with different ultraviolet light sources and optical filters. Crude oil calibrations performed using NIST SRM 2779 oil extracted in methanol with standards prepared in hexane. %Drop in concentration calculated comparing sample results tested 5 minutes and 10 days after preparation.

FIGURE 1

CHROMATOGRAM OF 10,000 PPM NIST SRM 2779 OIL EXTRACT IN HEXANE SOLVENT

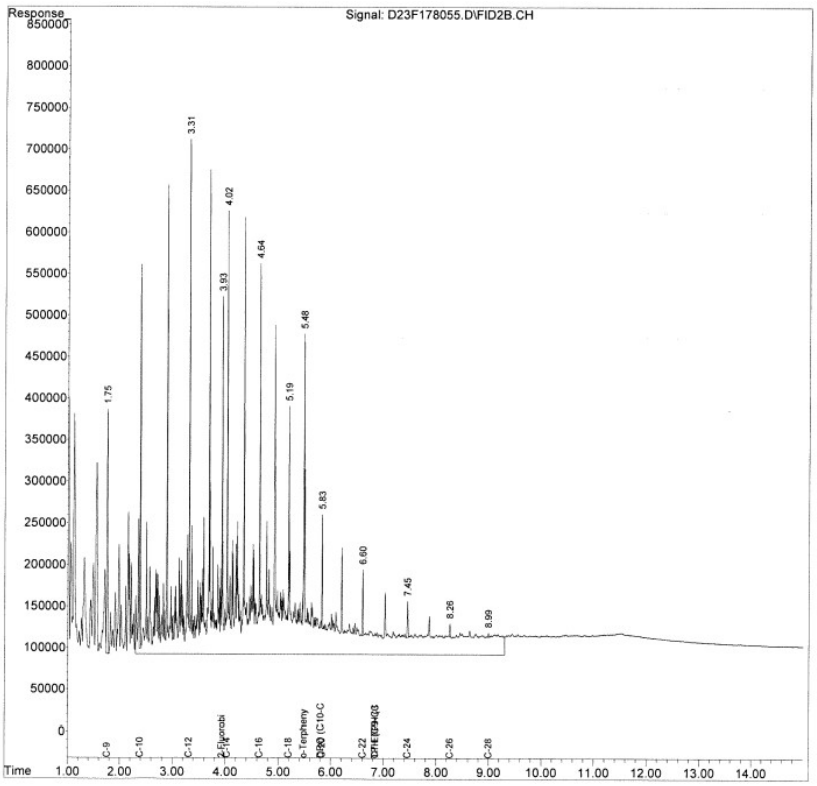


Laboratory GC/FID 8015C

TPH C9-C36 Concentration = 6,700 mg/Kg

FIGURE 2

CHROMATOGRAM OF 10,000 PPM NIST SRM 2779 OIL EXTRACT IN METHANOL SOLVENT



Laboratory GC/FID 8015C

TPH C9-C36 Concentration = 4,600 mg/Kg