METHOD 8670

POLYCYCLIC AROMATIC 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 polycyclic aromatic hydrocarbons (PAHs) in the C10 to C22 carbon range, specifically as the sum of the 16 PAH compounds on U.S. EPA's priority pollutant compound list plus 2-Methylnapthalene, for a total of 17 compounds which all have specific toxicity limits. This analysis is called PAHs or Target PAHs in this method. See list below with Chemical Abstract Service (CAS) Registry Numbers and chemical formula.

Target PAH Compounds:	CAS No.	Chemical Formula
Naphthalene	91-20-3	$C_{10}H_8$
2-Methylnaphthalene	91-57-6	$C_{11}H_{10}$
Acenaphthylene	208-96-8	$C_{12}H_8$
Acenaphthene	83-32-9	$C_{12}H_{10}$
Fluorene	83-73-7	$C_{13}H_{10}$
Phenanthrene	85-01-8	$C_{14}H_{10}$
Anthracene	120-12-7	$C_{14}H_{10}$
Fluoranthene	206-44-0	$C_{14}H_{10}$
Pyrene	129-00-0	$C_{16}H_{10}$
Benzo[a]Anthracene	56-55-3	$C_{18}H_{12}$
Chrysene	218-01-9	$C_{18}H_{12}$
Benzo[b]Fluoranthene	205-99-2	$C_{20}H_{12}$
Benzo[k]Fluoranthene	207-08-9	$C_{20}H_{12}$
Benzo[a]Pyrene	50-32-8	$C_{20}H_{12}$
Indeno[1,2,3-cd]Pyrene	193-39-5	$C_{22}H_{12}$
Dibenz[a,h]Anthracene	53-70-3	$C_{22}H_{14}$
Benzo[g,h,i]Perylene	191-24-2	$C_{22}H_{12}$

1.2 This method can be used to quantitate PAHs 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 PAH compounds, unless the contaminant in the sample matrix only contains one compound. In most cases, PAH contaminated samples contain many polycyclic aromatic compounds which co-fluoresce with UVF instrumentation. If analyzing individual analytes is required, refer to Methods 8270 or 8310 for guidance.

1.4 This method can also be used to quantitate PAH fractions or carbon ranges typically performed using Extractable Petroleum Hydrocarbon methods using GC instrumentation. This includes the compounds listed in Sec. 1.1, plus all other PAHs, including alkylated PAHs, in the C10 to C22 carbon range or other ranges up to C36 carbon weight. This analysis is called EPH Aromatics in this method. It should not be used for testing target PAHs since it will detect higher PAH concentrations due to differences in the optical figurations. See Sec. 6.2 for UVF instrument configurations for guidance. Refer to Massachusetts Department of Environmental Protection's Extractable Petroleum Hydrocarbons (MADEP EPH) Method or similar Gas Chromatography (GC) methods for guidance which separate polyaromatic and aliphatic hydrocarbon fractions. See Reference 7 for details about this method.

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

1.5 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, PAH 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, coal tars). This method was developed using commercially available certified reference standards suitable for most applications based on historical performance data compared to laboratory GC methods. Unlike GC methods, since UVF cannot detect individual compounds, this method is intended for screening purposes.

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 PAHs in samples can be measured using UVF instruments fitted with appropriate excitation and emission optical filters and light sources. Sensitivity varies depending on the

types and quantities of PAHs in a sample. In general, UVF is less sensitive to the smaller two and three ring aromatic compounds and more sensitive to the larger four, five and six ring compounds.

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 Target PAHs - 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 410-nm narrow band emission filter. Use of square quartz glass cuvettes is required.

6.2.2 Configuration for EPH Aromatics – 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.

6.2.3 Other configurations may be used. Method 8310, Sec. 4.6.3 for example, specifies a 254-nm UV detector coupled with 289-nm excitation and emission greater than 389-nm cutoff be used. This high performance liquid chromatography (HPLC) method uses fluorescence to detect the 16 priority pollutant PAH compounds.

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.

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.

7.2 Extraction solvents

This method has been validated using the solvents listed above. 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.

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.

7.3.1 Primary calibration standard – Use to establish baseline PAH measurement. Use a PAH mixture containing 17 compounds all at equal concentrations. Use for Target PAH analysis using configurations in Sec. 6.2.1 if comparing results to Method 8270 or other GC methods where the 17 regulated PAH compounds are reported. Use for EPH Aromatics analysis using configurations in Sec. 6.2.2 if comparing results to GC methods where EPH fractions are reported. Use this standard by default if the source of hydrocarbons in a sample is unknown.

7.3.2 Secondary calibration standard – Use a PAH mixture containing 16 compounds all at equal concentrations. Use for PAH analysis using configurations in Sec. 6.2.1 if comparing results to Method 8310 or other GC methods where the 16 regulated PAH compounds are reported. This standard fluoresces slightly stronger compared to the 17 compound mixture, producing slightly lower sample results.

7.3.3 Project-specific calibration standard – Use alternative standards when appropriate, including PAH standards supplied by proficiency testing providers to perform PAH 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.

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

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 compares the PAH composition in Certified Reference Materials (CRMs) from two manufacturers suitable for this method. These products include U.S. EPA's priority pollutant compounds with differences in composition. Percent PAH content was calculated by dividing each compound's concentration by the summation of all the compounds using data in References 1 thru 5 in Sec. 16. CRMs supplied by AccuStandard contain PAH mixtures with 17 or 16 compounds at equal concentrations. Composition of PAHs in CRMs supplied by Environmental Resource Associates (ERA) includes 16 compounds which vary from lot to lot or by part number and are developed to validate Method 8310. This data is provided for guidance purposes only.

13.4 Table 2 shows the fluorescence response comparing light to heavy PAH compounds using two certified reference materials for calibration and analysis. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.1. Fluorescence response was calculated by dividing sample readings by the concentration of the standard used and shown as a percentage. Fluorescence of individual compounds vary depending on the size and shape of each molecule. Fluorescence also varies depending on which standard is used for calibration. Calibration 1 performed using AccuStandard p/n DRH-006S, containing 17 PAH compounds at equal concentrations supplied in methylene chloride, with standards prepared in methanol for analysis. This CRM is used by Sitelab Corporation to prepare PAH calibration kits p/n CAL-060M in methanol and p/n CAL-060H in hexane. Calibration 2 performed using AccuStandard p/n ASM-098-5X, containing 16 PAH compounds at equal concentrations supplied in methylene chloride, with standards prepared in methanol for analysis. Standards used for Calibration 2 were prepared and analyzed at the same concentrations as standards used in Calibration 1. In this case, the 16 compound standard fluoresces 1.08 times stronger compared to the 17 compound standard due to the absence of 2-Methylnaphthalene. Relative percent difference (RPD) values show subtle variances analyzing 11 compounds and the two calibration standards. RPDs exhibited in most of the samples ranged from 6% to 8%. This data is provided for guidance purposes only.

13.5 Table 3 compares PAH spike recovery analysis testing drinking water, pond water and river water collected from local sources using two certified reference materials for calibration and analysis. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.1, calibrated using standards prepared in hexane. Spike recovery values testing all three types of water ranged from 88% to 118%. Spikes 1 and 3 contain a 17 PAH compound mixture in methanol using the same CRM used in Calibration 1. Spikes 2 and 4 contain a 16 PAH compound mixture in methanol using the same CRM used in Calibration 2. Water samples were spiked at two concentrations using 40 mL VOA vials and then extracted in hexane 24 hours after preparation. Clean, unspiked samples were also analyzed for comparison. Results exhibited show little difference using the two PAH mixtures; both are suitable for analysis. This data is provided for guidance purposes only.

13.6 Table 4 compares single laboratory accuracy and precision testing PAHs in water using two lots of ERA CRM 715 proficiency samples containing low concentrations of PAHs at varying concentrations. Data performed using analyzer configuration specified in Sec. 6.2.1, with calibrations performed using standards prepared in hexane using each CRM and Sitelab p/n CAL-060H for comparison. Water samples were spiked 1:1000 in clean tap water using 40

mL VOA vials and then extracted in hexane. Sample 1 was extracted 15 minutes after preparation; Sample 2 Duplicate was extracted 1 hour after preparation. PAH tests performed using the CRMs produced accurate recoveries (%R) close to 100%. Calibrations using Sitelab's Target PAH standard produced lower recoveries due to its different composition of PAHs. The laboratory mean result for Total PAHs in ERA's proficiency studies were calculated and shown for comparison. No QC or PT Performance Acceptance Limits are provided by ERA 715 for Total PAH concentrations; only Individual compound limits are provided. This data is provided for guidance purposes only.

13.7 Table 5 compares single laboratory accuracy and precision comparing two UVF analyzers testing PAHs in soil using ERA CRM 722 proficiency sample. Both analyzers used configurations specified in Sec. 6.2.1, but were manufactured one year apart and calibrated using standards made from different lot numbers. Samples were prepared in duplicate containing 10-g each extracted in 20 mL methanol for 24 hours. PAH tests performed produced accurate recoveries (%R) >50% and results were similar with both instruments. The laboratory mean result for Total PAHs in ERA's proficiency study was calculated and shown for comparison. No QC or PT Performance Acceptance Limits are provided by ERA 722 for Total PAH concentrations; only individual compound limits are provided. This data is provided for guidance purposes only.

13.8 Table 6 compares PAH matrix spike recovery analysis testing soil and clay collected from local sources, play sand and charcoal briquets purchased from retail stores, burnt charcoal ash from the briquets and ERA CRM 570 containing petroleum hydrocarbons made with vacuum pump oil. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.1, calibrated to Sitelab p/n CAL-060M. Samples were spiked and analyzed at three concentrations. Spike 1 and Spike 2 samples prepared using a 500 ppm stock solution dissolved in hexane using AccuStandard p/n DRH-006S. Spike 3 samples prepared using AccuStandard p/n DRH-006S (undiluted), supplied in methylene chloride at 17,000 ppm. Spiked aliquots of 5, 10 and 200 ppm concentrations were added to 5-g samples and extracted in 20 mL methanol for 24 hours. Unspiked samples were also prepared and tested using the same volumes and conditions as the spiked samples. Percent recovery (%R) values account for sample concentrations without spike added. PAH tests performed in the sand, soil, clay and ERA samples produced accurate recoveries from 90% to 104%. Poor recoveries were observed in the charcoal and ash samples due to poor extraction efficiency. These samples were chosen to illustrate the limitations to this method. This data is provided for guidance purposes only.

13.9 Table 7 shows spike recovery analysis using a laboratory control sample testing Target PAHs in clean soil, clay and beach sand collected from local sources and two lots of ERA CRM 570 containing petroleum hydrocarbons made with vacuum pump oil. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.1, calibrated to Sitelab p/n CAL-060M. Samples were spiked with crude oil at two concentrations using National Institute of Standards & Technology (NIST), Standard Reference Material (SRM) 2779. Low spikes prepared using a 10,000 ppm oil extract in hexane solvent. High spikes prepared using the oil. Spiked aliquots were added to 10-g samples and extracted in 20 mL methanol for 24 hours. Unspiked samples were prepared and tested using the same volumes and conditions as the spiked samples. Percent recovery values account for concentrations in samples with no spike added. LCS standards were prepared using the 10,000 ppm oil extract in hexane with dilutions prepared in methanol for analysis. PAH tests performed produced accurate recoveries from 65% to 93%. In this case, the oil fluoresces 33 times lower compared to the calibration response and is within the acceptance criteria established by the laboratory. See Reference 6 in Sec. 16 for PAH composition in the oil. This data is provided for guidance purposes only

13.10 Table 8 shows historical soil data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.1, calibrated to Sitelab p/n CAL-060M. Examples of PAH results in soils, sediments and other solids from different sites with different sources of hydrocarbon contamination are compared to confirmatory results performed by certified laboratories using Method 8270 or the MADEP EPH Method testing split samples. Concentrations of the 17 compounds were added together to report Total PAH by the labs. Samples 1 thru 21 were prepared using 5 grams of sample extracted in 10 mL methanol for 5 to 10 minutes. River sediment samples were adjusted for moisture content performed by the laboratories. Samples 22 and 23 with high PAH content were prepared using 1 gram of sample extracted in 20 mL methanol for 24 hours. Relative percent difference (RPD) values were less than 50% in this data set. This data is provided for guidance purposes only.

13.11 Table 9 shows the fluorescence response of PAH compounds and fuel oils analyzed for EPH Aromatics and Target PAHs with response factors exhibited for comparison. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.2, calibrated using the same 17 compound PAH standard used for measuring Target PAHs. AccuStandard PAH compounds, kerosene and No. 2 fuel oil were supplied in methanol and diluted further in methanol for analysis. AccuStandard No. 4 and No. 6 fuel oils were supplied in hexane and diluted in methanol for analysis. The NIST SRM 2779 crude oil was extracted I hexane and diluted in methanol for analysis. Fluorescence response was calculated by dividing sample readings by the concentration of the standard used and shown as a percentage. EPH Aromatics is more sensitive to the lighter PAH compounds, producing stronger fluorescence compared to Target PAH analysis. EPH Aromatics is less sensitive to the heavier PAH compounds, producing lower fluorescence compared to Target PAH analysis. This is due to the different optical emission filters used. The fluorescence response in the fuel oils also varies due to each fuel's PAH composition. Heavy fuel oils contain more PAHs and fluoresce stronger compared to lighter fuel oils. This data is provided for guidance purposes only.

13.12 Table 10 compares accuracy testing EPH Aromatics in soils collected from two fuel oil sites compared to the unadjusted C11 – C22 aromatic hydrocarbon fraction performed by certified laboratories using the MADEP EPH Method. Data performed by a single laboratory with analyzer configuration specified in Sec. 6.2.2, calibrated using the same 17 compound PAH standard used for measuring Target PAHs. Soils were analyzed on-site using 5-g samples extracted in 10 mL methanol for 5 to 10 minutes. Samples 1 to 3 were collected from a subsurface commingled plume with diesel fuel, No. 2 fuel oil and No. 6 fuel oil. Samples 4 to 6 were collected from a No. 6 fuel oil release only. Example results show relative percent difference (RPD) values were less than 50% testing soils from low to high concentrations.

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. AccuStandard, Certified Reference Material DRH-006S, “Proposed DEP(MA) PAH Mix”, Certificate of Analysis, Lot No. 223071038, July 12, 2023.

2. AccuStandard, Certified Reference Material ASM-098-5X, “PNA Mix”, Certificate of Analysis, Lot No. 220011364-01, February 15, 2022.

3. Environmental Resource Associates, Certified Reference Material 715, “Low-Level PAHs in Water,” Certificate of Analysis, Lot No. P318-715, October 4, 2021.

4. Environmental Resource Associates, Certified Reference Material 715, “Low-Level PAHs in Water,” Certificate of Analysis, Lot No. P321-715, January 25, 2022.

5. Environmental Resource Associates, Certified Reference Material 722, “Low-Level PAHs in Soil,” Certificate of Analysis, Lot No. D115-722, December 1, 2021.

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

7. 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

COMPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)
IN CERTIFIED REFERENCE MATERIALS USED FOR UVF ANALYSIS

Compounds Listed in C10 – C22 Range	AccuStandard DRH-006S 17 Compounds PAH Content %	AccuStandard ASM-098-5X 16 Compounds PAH Content %	ERA 715 PAHs in Water Lot P318-715 PAH Content %	ERA 715 PAHs in Water Lot P321-715 PAH Content %	ERA 722 PAHs in Soil Lot D115-722 PAH Content %
Naphthalene	5.9	6.3	10.1	11.0	2.7
2-Methylnaphthalene	5.9	0	0	0	0
Acenaphthylene	5.9	6.3	20.7	25.1	10.0
Acenaphthene	5.9	6.2	10.1	14.7	14.8
Fluorene	5.9	6.2	11.8	3.3	6.8
Phenanthrene	5.9	6.2	5.9	5.5	12.7
Anthracene	5.9	6.3	2.0	4.4	7.8
Fluoranthene	5.9	6.2	6.5	2.3	5.0
Pyrene	5.9	6.3	7.2	3.1	6.5
Benzo[a]Anthracene	5.9	6.2	1.8	4.3	7.3
Chrysene	5.9	6.2	6.2	5.2	6.3
Benzo[b]Fluoranthene	5.9	6.3	1.2	3.0	2.1
Benzo[k]Fluoranthene	5.9	6.2	1.7	5.2	2.1
Benzo[a]Pyrene	5.9	6.2	6.0	1.3	3.3
Indeno[1,2,3-cd]Pyrene	5.9	6.3	2.1	3.0	2.5
Dibenz[a,h]Anthracene	5.9	6.3	5.4	2.8	3.5
Benzo[g,h,i]Perylene	5.9	6.2	1.2	5.6	6.6
Total PAH Content %	100	100	100	100	100

This data is provided for guidance purposes only. Certified Reference Materials (CRMs) supplied by AccuStandard contain PAH mixtures with 17 or 16 compounds at equal concentrations. Composition of PAHs in CRMs supplied by Environmental Resource Associates (ERA) vary from lot to lot or by part number. ERA's CRMs are developed to validate Method 8310 and are suitable to validate this method.

TABLE 2

FLUORESCENCE RESPONSE OF POLYCYCLIC AROMATIC COMPOUNDS IN METHANOL COMPARING TWO REFERENCE STANDARDS USED FOR CALIBRATION AND ANALYSIS

UVF Analyzer with PAH Optics, Calibrations and Analysis in Methanol Solvent Example Compounds in C10 – C22 Range	Molecular Weight ($g \cdot mol^{-1}$)	Aromatic Rings per Compound	Calibration 1: 17 PAHs, AccuStandard DRH-006S Fluorescence Response (%)	Calibration 2: 16 PAHs, AccuStandard ASM-098-5X Fluorescence Response (%)	RPD
Naphthalene, C10	128	2 Rings	0.07	0.06	15.4
2-Methylnaphthalene, C11	142	2 Rings	0.20	0.18	10.5
Phenanthrene, C14	178	3 Rings	11.7	10.8	8.0
Anthracene, C14	178	3 Rings	475	440	7.6
Fluoranthene, C16	202	4 Rings	12.5	11.7	6.6
Pyrene, C16	202	4 Rings	13.8	12.8	7.5
Benzo[a]Anthracene, C18	228	4 Rings	94	87	7.7
Chrysene, C18	228	4 Rings	38	35	8.2
Benzo[k]Fluoranthene, C20	252	5 Rings	645	600	7.2
Benzo[a]Pyrene, C20	252	5 Rings	330	308	6.9
Dibenz[a,h]Anthracene, C22	278	5 Rings	11.0	10.3	6.6
17 Compound PAH Mixture Standard Response:			100	93	7.3
16 Compound PAH Mixture Standard Response:			108	100	7.7

This data is provided for guidance purposes only. The 16 compound mixture fluoresces 1.08 times stronger compared to the 17 compound mixture due to the absence of 2-Methylnaphthalene. Relative percent difference (RPD) values show subtle variances analyzing 11 PAH compounds and the two calibration standards. RPDs exhibited in most of the samples ranged from 6% to 8%.

TABLE 3

SPIKE RECOVERY ANALYSIS TESTING PAHS IN WATER COMPARING TWO REFERENCE STANDARDS PREPARED IN HEXANE USED FOR UVF CALIBRATION AND ANALYSIS

UVF Analyzer with PAH Optics, Calibrations and Analysis in Hexane Solvent	Spike Conc. µg/L	Calibration 1: 17 PAH Compounds, AccuStandard DRH-006S (Sitelab CAL-060H) Result µg/L	%Recovery	Calibration 2: 16 PAH Compounds, AccuStandard ASM-098-5X Result µg/L	%Recovery
5 Drinking Water Samples					
Unspiked Sample	0	0.0		0.0	
Spike 1, 17 PAHs	50	51	102%	48	96%
Spike 2, 16 PAHs	50	59	118%	56	112%
Spike 3, 17 PAHs	100	107	107%	101	101%
Spike 4, 16 PAHs	100	110	110%	105	105%
5 Pond Water Samples					
Unspiked Sample	0	0.2		0.2	
Spike 1, 17 PAHs	50	54	108%	51	102%
Spike 2, 16 PAHs	50	51	102%	52	104%
Spike 3, 17 PAHs	100	101	101%	95	95%
Spike 4, 16 PAHs	100	101	101%	95	95%
5 River Water Samples					
Unspiked Sample	0	0.5		0.5	
Spike 1, 17 PAHs	50	46	91%	44	87%
Spike 2, 16 PAHs	50	48	95%	46	91%
Spike 3, 17 PAHs	100	101	101%	96	96%
Spike 4, 16 PAHs	100	105	105%	99	99%

This data is provided for guidance purposes only. Spike recovery values testing three types of water ranged from 88% to 118%. Spikes 1 and 3 contain a 17 PAH compound mixture in methanol using the same Certified Reference Material (CRM) in Calibration 1. Spikes 2 and 4 contain a 16 PAH compound mixture in methanol using the CRM in Calibration 2. Results exhibited show little difference using the two PAH mixtures; both are suitable for analysis.

TABLE 4

POLYCYCLIC AROMATIC HYDROCARBONS IN WATER TESTING TWO LOTS OF ERA CRM 715 PROFICIENCY SAMPLES CONTAINING LOW CONCENTRATIONS OF PAHS

UVF Analyzer with PAH Optics, Calibrations and Analysis in Hexane Solvent	Sample 1 µg/L	Sample 2 Duplicate µg/L	Average Result µg/L	Total 16 PAHs Certified Value µg/L	%R
Lot 1 Water Study:					
1. PAH Water Standard, ERA 715, Lot P318-715	56.0	62.0	59.0	60.9	97%
2. Target PAHs Standard, Sitelab CAL-060H	30.0	32.0	31.0	60.9	51%
ERA Proficiency Study, Lot P318-715 Total 16 PAH Compounds Mean Result: (Based on 46 lab tests)			45.2	60.9	74%
Lot 2 Water Study:					
1. PAH Water Standard, ERA 715, Lot P321-715	69.0	73.0	71.0	70.5	101%
2. Target PAHs Standard, Sitelab CAL-060H	50.0	52.0	51.0	70.5	72%
ERA Proficiency Study, Lot P321-715 Total 16 PAH Compounds Mean Result: (Based on 37 lab tests)			57.4	70.5	81%

This data is provided for guidance purposes only. UVF calibrations performed using two CRMs supplied in methanol by Environmental Resource Associates (ERA), containing 16 PAH compounds at varying concentrations, with calibration standards prepared in hexane. Additional calibrations performed using Sitelab CAL-060H for comparison.

Samples spiked 1:1000 in tap water using ERA's 715 standards and extracted in hexane for analysis. Sample 1 was extracted 15 minutes after preparation. Sample 2 was extracted 1 hour after preparation.

PAH tests performed produced accurate recoveries >50%. Calibrations using Sitelab's Target PAH standard exhibited lower recoveries due to its different composition of PAHs. No QC or PT Performance Acceptance Limits are provided by ERA 715 for Total PAH concentrations; only individual compound limits are provided.

TABLE 5

ACCURCY AND PRECISION USING TWO UVF ANALYZERS TESTING TARGET PAHS IN SOIL USING ERA CRM 722 PROFICIENCY SAMPLE

UVF with PAH Optics, Calibrations and Analysis in Methanol Solvent	Sample 1 ug/Kg	Sample 2 Duplicate ug/Kg	Average Result ug/Kg	Total 16 PAHs Certified Value ug/Kg	%R
Analyzer 1:					
PAH Factory Calibration, Sitelab CAL-060M, Lot 1	4,400	5,000	4,700	5,838	81%
Analyzer 2:					
PAH Factory Calibration, Sitelab CAL-060M, Lot 2	4,360	4,800	4,580	5,838	78%
	ERA Proficiency Study, Lot D115-722 Total 16 PAH Compounds Mean Result: (Based on 39 lab tests)		4,029	5,838	69%

This data is provided for guidance purposes only. Two soil samples containing 10-g each were extracted in 20 mL methanol solvent for 24 hours. PAH tests performed produced accurate recoveries >50%. No QC or PT Performance Acceptance Limits are provided by ERA 722 for Total PAH concentrations; only individual compound limits are provided.

TABLE 6

SPIKE RECOVERY ANALYSIS TESTING SOILS AND OTHER SOLID MATRICES IN METHANOL SPIKED WITH 17 COMPOUND PAH MIXTURE AT THREE CONCENTRATIONS

UVF with PAH Optics, Target PAHs using Sitelab CAL-060M	Sample with No Spike mg/Kg	Spike 1 5 ppm mg/Kg	%R	Spike 2 10 ppm mg/Kg	%R	Spike 3 200 ppm mg/Kg	%R
Play Sand	0.02	5.2	104%	10.4	104%	202	101%
Sandy Loam Soil	0.06	4.8	95%	9.6	95%	184	92%
Clay	0.04	4.6	91%	9.8	98%	180	90%
ERA 570 TPH Soil	1.6	6.2	92%	11	94%	182	90%
Charcoal Grill Briquets	11	13	40%	14	30%	82	36%
Charcoal Grill Ash	0.08	0.12	0.8%	0.12	0.4%	3.8	1.9%

This data is provided for guidance purposes only. Samples contained 5-g each extracted in 20 mL methanol solvent for 24 hours. Percent recovery (%R) values account for sample concentrations without spike added. Most recoveries (%R) exhibited were >50%. Poor recoveries observed in the charcoal and ash samples due to matrix effects or interferences.

Environmental Resource Associates (ERA) CRM 570 Total Petroleum Hydrocarbons (TPH) in Soil, Lot D118-632, contains 579 mg/Kg TPH by Gravimetric and 712 mg/Kg TPH by Infrared. This product contains vacuum pump oil.

TABLE 7

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

Low Oil Spiked Samples:	Sample with No Spike mg/Kg	Spike 1 100 ppm mg/Kg	100 ppm LCS Oil Standard Response mg/Kg	%Recovery
Beach Sand	0.04	2.8	3.0	92%
Sandy Loam Soil	0.06	2.6	3.0	85%
Clay	0.04	2.2	3.0	72%
ERA 570 TPH Soil 1	1.6	4.4	3.0	93%
ERA 570 TPH Soil 2	1.8	4.6	3.0	93%
Target PAHs LCS Acceptance Criteria: (single laboratory in-house QC study)			2.7 – 3.3	

High Oil Spiked Samples:	Sample with No Spike mg/Kg	Spike 2 5,000 ppm mg/Kg	5,000 ppm LCS Oil Standard Response mg/Kg	%Recovery
Beach Sand	0.04	140	150	93%
Sandy Loam Soil	0.06	130	150	87%
Clay	0.04	130	150	87%
ERA 570 TPH Soil 1	1.6	130	150	86%
ERA 570 TPH Soil 2	1.8	100	150	65%
Target PAHs LCS Acceptance Criteria: (single laboratory in-house QC study)			135 – 165	

This data is provided for guidance purposes only. Study performed using UVF analyzer with PAH optics calibrated to Sitelab CAL-060M in methanol. The LCS standard fluoresces 33 times lower due to the different composition of PAH compounds in the oil. PAH tests performed produced accurate recoveries >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 8

EXAMPLE PAH RESULTS IN SOILS, SEDIMENTS AND OTHER SOLIDS FROM DIFFERENT CONTAMINATED SITES COMPARED TO LABORATORY GC RESULTS

Site Description, Matrix Contaminant	Sample Number	UVF Target PAHs mg/Kg	Lab GC/MS Total PAHs mg/Kg	RPD
Petroleum Tank Farm	1	3	ND <1	---
Soils, Mixed Fuel Oil Site	2	75	80	7%
	3	97	82	17%
	4	180	130	32%
	5	370	350	6%
	6	455	682	40%
Underground Storage Tank	7	8	6.8	16%
Soils, Diesel Fuel Site	8	17	15	13%
	9	60	57	5%
Underground Storage Tank	10	4.4	3.0	38%
Soils, Gasoline Site	11	7.7	6.0	25%
	12	30	21	35%
U.S. AFB Power Plant	13	9	10	11%
Soils, Coal Ash Site	14	16	13	21%
	15	30	21	35%
MGP Coal Tar Site	16	110	113	3%
River Sediments, Colorado	17	600	666	10%
	18	1,500	1,200	22%
MGP Coal Tar Site,	19	44	46	4%
River Sediments, North Carolina	20	184	174	6%
Urban Fill, Soil with Asphalt and Coal Ash	21	61	69	12%
Dry Pavement Sealer, Ethylene Cracked Residue	22	26,000	25,585	2%
Dry Pavement Sealer, Refined Coal Tar	23	70,000	77,779	11%

This data is provided for guidance purposes only. UVF performed using configurations in Sec. 6.2.1., calibrated to Sitelab CAL-060M in methanol. Confirmatory results performed by certified laboratories using U.S. EPA Method 8270 or MADEP EPH Method testing split samples. Concentrations of the 17 compounds were added together to report Total PAH.

TABLE 9

FLUORESCENCE RESPONSE OF PAH COMPOUNDS AND FUEL OILS COMPARING EPH AROMATICS AND TARGET PAHS CALIBRATED TO 17 COMPOUND STANDARD

Analyzers Calibrated to Sitelab CAL-060M	UVF-Trilogy with EDRO Optics	UVF-Trilogy with PAH Optics	
Example PAHs with Carbon Size and Fuel Oils Tested for Comparison	EPH Aromatics, Fluorescence Response (%)	Target PAHs, Fluorescence Response (%)	Response Factor Exhibited (RF)
Naphthalene, C10	30	0.07	434
2-Methylnaphthalene, C11	55	0.20	275
Phenanthrene, C14	320	11.7	27
Anthracene, C14	370	475	0.78
Benzo[k]Fluoranthene, C20	80	645	0.12
Benzo[a]Pyrene, C20	33	330	0.10
No. 2 Fuel Oil	25	0.70	36
No. 4 Fuel Oil	50	5.0	10
No. 6 Fuel Oil	80	10.0	8.0
Light Crude Oil, NIST SRM 2779	28	3.0	9.3

This data is provided for guidance purposes only. Samples analyzed using configurations in Sec. 6.2.1 and 6.2.2.

TABLE 10

EPH AROMATICS IN SOILS FROM FUEL OIL SITES COMPARED TO MADEP EPH C11-C22 AROMATIC HYDROCARBONS PERFORMED BY CERTIFIED LABORATORIES

Example Soils from NAPL Plume Investigations with Low to High Concentrations	Sample Number	UVF EPH Aromatics mg/Kg	Lab GC/FID EPH Aromatics mg/Kg	RPD
Tank Farm, Massachusetts	1	1,100	1,130	3%
Mixed Fuel Oil Site	2	3,585	4,600	25%
	3	7,200	6,820	5%
Wire Factory, Connecticut	4	5,250	4,800	9%
No. 6 Fuel Oil Site	5	9,100	11,000	19%
	6	23,600	21,000	12%

This data provided is for guidance purposes only. UVF calibrated to Sitelab CAL-060M using EDRO Optics.