

Review Article

Analytical Methods for the Determination of the Distribution of Total Petroleum Hydrocarbons in the Water and Sediment of Aquatic Systems: A Review

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Several methods of extraction and analytical determination for total petroleum hydrocarbons (TPHCs) in aqueous and solid samples are reviewed. Infrared spectroscopy is one of the efficient methods that are being replaced today pursuant to getting rid of some halogenated solvents classified as ozone-depleting substances. The gravimetric method which uses n-hexane as an extraction solvent for the determination of oil and grease, as well as the nonpolar materials, has become a preferred choice, despite being not suitable for volatiles because of the mandatory evaporation step. Other frequently used methods include gas chromatography with a flame ionization detector (FID) or mass spectrometric detector (MSD) which has the capacity to reveal the type of hydrocarbons present and is applicable to both volatile and semivolatile samples. Ultraviolet fluorescence is another method that is available both as a portable field device and as off-site laboratory equipment. Each of the methods has its own advantages and disadvantages; hence, the choice of method is guided by the type of data needed as discussed in detail in this review. The distribution of TPHC in water and sediments across the globe and the factors influencing the distribution were also reviewed.

1. Introduction

Petroleum hydrocarbons (PHCs) are prominent among organic contaminants which are frequently disposed into the marine environment in lower concentrations in the form of urban runoffs, automobile wastes, stormwater, industrial effluents, or domestic wastes [1–3] and occasionally in higher concentrations as a major oil spill [4, 5]. The main constituents of these PHCs are degraded crude oils, combusted fossil fuels, and normal alkanes [6, 7]. They are generally less soluble in water but are readily adsorbed onto particulate matter and are subsequently scavenged to the bottom sediment which has become a reservoir for several hydrophobic contaminants. The danger in the sedimentation of these organic pollutants is their tendency to accumulate and bioconcentrate over time in aquatic organisms [8–10].

Total petroleum hydrocarbons (TPHCs) is the term generally used to describe the amount of petroleum-based hydrocarbon extracted and quantified by a particular method in an environmental matrix [11, 12]. TPHC analytical methods vary in scope to a great extent, with each providing results within a particular range, while some are nonspecific. Hence, understanding how the analysis was carried out is very crucial for correct interpretation of the results obtained. Methods with different extraction efficiencies could produce different TPHC concentrations for the same sample [13, 14]. Hence, results generated using different procedures are always difficult to compare because different calibration standards and extracting solvents are involved [6].

Petroleum hydrocarbons consist majorly of three groups of compounds, namely, alkanes, alkenes, and aromatics [15]. Alkanes are the key components of many refined petroleum

products (e.g., gasoline, diesel fuel, kerosene, jet fuel, and heating oil) and are subdivided into several classes which include the following: linear alkanes (n-alkanes), branched alkanes, isoprenoids, cycloalkanes (e.g., steranes and triterpanes), and unresolved complex mixtures (UCM) which are difficult to resolve by capillary column gas chromatography [6, 16]. The presence of UCM in chromatograms is usually an indication of petroleum degradation. They are commonly found in the high-molecular-weight range of the n-alkanes but are sometimes present in the low molecular range as well [17, 18].

TPHC is sometimes determined as the sum of concentrations of n-alkanes and UCM [19] or as the total concentration of all hydrocarbons eluting from n-nonane (C9) to n-hexatriacontane (C36) excluding the priority polycyclic aromatic hydrocarbons [20]. They are mostly found in the higher-molecular-weight range of the hydrocarbons and sometimes also in the low-molecular-weight range [21]. TPHC could also be measured as the sum of aliphatic and aromatic hydrocarbons, especially those in the following groups: C9 to C18 (aliphatic), C19 to C36 (aliphatic), and C11 to C22 (aromatic) [22–24].

Total petroleum hydrocarbons (TPHCs) themselves may not be a direct pointer of hazard to humans or the environment [13, 25], but their presence indicates the health status of the water body and is also used for source tracking of the contaminants in the coastal waters and sediments [26, 27]. In this paper, we review the existing methods of extraction for petroleum hydrocarbon in water and solid samples, compare methods of final determination, and assess the levels of petroleum hydrocarbons in the aquatic environments across the globe and the available tools for source tracking using n-alkanes as reference compounds.

2. Physicochemical Properties

2.1. Boiling Points. Generally, the boiling point of hydrocarbons (HCs) increases as the number of carbon atoms increases. For n-alkanes, an increase of approximately 20°C is observed for every addition of new carbon atom to the chain. PAHCs are characterized by higher melting points and boiling points than their corresponding n-alkanes and therefore they are solid in nature [28].

2.2. Solubility, Volatility, and Persistence. The extent of interaction of hydrocarbon structures with water depends on their degree of polarity. Aliphatic hydrocarbons are generally less polar and are therefore less soluble in water compared to their corresponding aromatic counterparts. For instance, the solubility of aliphatic hydrocarbons in the range of C5–C6 is 36 mg/L while aromatic hydrocarbons in the same range have solubility as high as 220 mg/L. The most soluble components of the aromatic hydrocarbons are the lower-molecular-weight compounds. Therefore, solubility decreases as the number of the aromatic rings and molecular-weight increase. On the other hand, the aliphatic HCs are relatively more volatile than the aromatic HCs with a similar number of carbon atoms [29]. Nearly all the normal alkanes with carbon number less than 15 are lost by volatilization in the early days of spillage

while those with carbon number greater than 20 are lost some weeks later [13, 30]. Lower weight hydrocarbons are less persistent in the environment unlike the high-molecular-weight hydrocarbons. Therefore, persistence of petroleum hydrocarbons rises as the boiling point of the compound increases [28].

2.3. Toxicity and Microbial Degradation. Aromatic hydrocarbons are considered to be relatively more toxic and more resistant to microbial degradation than the corresponding normal alkanes, isoalkanes, cycloalkanes, and the unsaturated aliphatic hydrocarbons [5, 31]. The degree of toxicity of contaminants in water will to a large extent depend on their level of solubility [28]. Microbial degradation of hydrocarbons is a function of many factors which include the level of dissolved oxygen, pH, and microbial population in the environment. The population of the degrading bacteria can be lower in an unpolluted environment but can drastically increase when in contact with spilled petroleum substances [32–36].

The rate of susceptibility of hydrocarbons to microbial degradation differs from one class to another [37, 38] and bacteria can degrade aliphatic, alicyclic, and aromatic hydrocarbons of low to moderate weights at a higher rate when the environmental conditions are very ideal. However, the rate of biodegradation decreases as the resistance due to the increase in the molecular weight of the compounds increases [39]. The typical decreasing order of biodegradation is given as follows: n-alkanes > branched alkanes > low-molecular-weight aromatics > cyclic alkanes > high-molecular-weight aromatics. Aromatic hydrocarbons are generally less biodegradable than the corresponding aliphatic hydrocarbons [5, 37, 38].

Oxygenases can convert alkanes to alcohol by the process of degradation. The alcohol can be oxidized to aldehyde and then to fatty acids which can subsequently be utilized in the β -oxidation of the aliphatic chain. In a similar manner, cycloalkanes can be degraded to cyclic alcohol by oxidases and then dehydrogenated to ketone. Similarly, aromatic hydrocarbons can be transformed to an epoxide through the action of oxygenases. The product can then be hydrated to *trans*-dihydrodiols which are later oxidized to catechols. Catechol can later be oxidized further to muconic acid or 2-hydroxymuconic semialdehyde [40] which can finally be degraded to yield organic acids that are used by microorganisms for cell synthesis and energy production [41].

3. Sources of Petroleum Hydrocarbons in the Marine Environment

Petroleum hydrocarbons in the marine environment come from natural (biogenic or diagenetic) and anthropogenic (petrogenic or pyrogenic) sources [42]. Biogenic source hydrocarbons refer to those hydrocarbons produced by living organisms (e.g., planktons, algae, and bacteria) or through biological processes involving terrestrial plants. Examples include C23–C33 aliphatic hydrocarbons which are largely produced by the terrestrial plant detritus and odd-numbered n-alkanes (C15, C17, and C19) from biogenic marine input

which are usually available in low quantity [43]. Hydrocarbons from diagenetic sources are those produced as a result of physical and geochemical changes gone through by a sediment after its initial deposition as it changes into rock. They enter marine water mostly by natural seepage [44].

The anthropogenic hydrocarbons are usually more in the environment than the natural ones. They are commonly generated from various human activities like industrialization, urbanization, transportation, oil utilization, operations and storage, shipping, and fishing [45, 46]. Abundance of C16, C18, and C20 in most cases suggests oil spillage [18] from tanks and oil pipelines constructed to transfer crude oil from one place to another [44]. For anthropogenic derived hydrocarbons, the level of odd-numbered alkanes is almost equal to that of the even-numbered ones, usually in the ratio 1:1 [43]. In the early 1980s, it was concluded that approximately 10% of the crude oil in the marine environment comes from natural oil seeps, and another 27% comes from oil production, refining, and transportation, while the balance of 63% originates from urban and river runoff, atmospheric emission, and municipal and industrial discharges, among others [44].

4. Sample Collection and Preservation

Sample collection and preparation strategies are very crucial in the analysis of petroleum hydrocarbons in the environment [47]. The sample must be collected without contamination and must be wholly representative of the environmental medium where it was taken [11, 13]. The analyst must ensure that no bias or error is introduced into the samples during and after the collection. The sampling equipment must be thoroughly cleaned in between sampling points to avoid cross-contamination and the sample must be homogeneous. A minimum of one duplicate field sample is required in good practice for aqueous samples and space should be left for air above the sample to prevent overflow [47, 48].

The use of 1-liter amber glass bottles with Teflon-lined screw cap for aqueous sample collection is recommended. Samples are to be preserved at the time of collection with concentrated HCl or H₂SO₄ to pH < 2 and held at 4°C immediately after collection until extracted within 14 days of collection. However, unpreserved samples must be extracted within 7 days [23, 48, 49]. Soil or sediment samples are to be collected with a grab or core sampler or any other equipment as found appropriate in 120 mL wide-mouth glass jar or vessel of any other sizes, depending on the quantity of samples needed for the analysis [47]. The samples must be cooled to 4°C and extracted within 14 days of collection. Both the aqueous and the soil/sediment extracts must be analyzed within 40 days of extraction [11, 49]. A volume of 400 mL is the smallest aqueous sample size allowed for this analysis provided that the solvent/sample ratio is upheld [23].

Soil or sediment samples can be otherwise preserved at 4 ± 2°C at the time of collection and frozen thereafter at -10°C within 48 hours. The sample must be extracted not later than 14 days when thawed and analyzed within the next 40 days. The frozen samples can be held for up to a year before analysis if need be but must be extracted within 24 hours of defrosting [48].

5. Extraction and Cleanup Methods for TPHC in Water and Sediments

The most commonly used extraction methods for the isolation of the semivolatile compounds from water, soil, and sediment samples prior to analytical determination are discussed below.

5.1. Water Samples. The most commonly used extraction method for TPHC in aqueous samples is the EPA 3510 liquid-liquid extraction [5, 50, 51]. Other available methods include continuous liquid-liquid extraction [11], solid phase extraction [51], vortex extraction [52], and microextraction [53].

The liquid-liquid extraction (LLE) technique involves the use of a separatory funnel for multiple extraction of the sample with an organic solvent of choice with the intent of achieving good recovery of the desired analytes. The technique requires strong shaking of the liquid sample with an organic solvent in a funnel shaped piece of glassware for a couple of minutes, followed by the separation of the organic layer (extract) from the aqueous phase. The extract is then filtered through a desiccant to remove moisture before a final concentration prior to the analytical procedure. The method is however labor-intensive and solvent consuming [11, 54]. Another method is the EPA 3520, the continuous liquid-liquid extraction (CLLE) which involves continuous recycling of fresh organic solvent in the form of droplets which are passed through the water sample. It is very efficient, requires less attention of the operator, and consumes very little volume of solvent. CLLE is very good for samples containing emulsion-forming solids but has few disadvantages. It consumes more time (18–24 hours) than the conventional LLE (EPA 3510) and has a tendency to degrade the thermally unstable compounds, as well as lose some volatile ones in the process [11] (http://www.chemistry.sc.chula.ac.th/course_info/2302548/Wk3.pdf).

Solid phase extraction (SPE, EPA Method 3535) involves passing of a water sample through a cartridge containing an adsorbent like silica or alumina in which analytes are retained and afterwards eluted with a small portion of organic solvent [11, 55]. It has better extraction efficiency and uses lesser solvent and glassware compared to LLE and CLLE. Sample transfer in SPE is very minimal, guaranteeing little or no cross-contamination [56]. Many laboratories are still using LLE and SPE today, even though they are time-consuming, because they are relatively inexpensive, simple, and highly efficient [57].

5.2. Solvent Selection. The choice of solvent used for organic extraction in relation to the type of material extracted determines to a very large extent the efficiency of such an extraction process. A good extracting solvent should have low boiling point, low miscibility with water, and high solubility for the desired analytes [58]. Other criteria to be considered in the choice of solvents include cost, toxicity, spectral qualities, availability, method regulations, and extraction efficiency [11]. Organic contaminants were in time past extracted with halogenated solvents like Freon 113 (trichlorotrifluoroethane) which were less toxic to humans and possess good infrared

spectral qualities. However, they are presently being phased out globally because of their implication in ozone layer depletion. Possible replacements for these solvents include dichloromethane, pentane, n-hexane, tetrachloroethene, and carbon tetrachloride [11, 13, 59].

Extraction efficiency of the organic analytes in aqueous samples is frequently monitored by the addition of surrogate standard solution (e.g., 1-chlorooctadecane for the n-alkanes; 2-fluorobiphenyl for the PAHs) to the sample matrix before extraction. Many laboratories are also performing matrix spikes with the intent of determining whether the compounds of interest are retained in the water, soil, or sediment matrices [60].

5.3. Solid Samples. The most frequently used methods for the extraction of soil and sediment samples prior to their analytical determination include conventional Soxhlet extraction [27, 61], ultrasonication [52, 62], vortex/mechanical shaking [63], accelerated solvent extraction [5, 64], and supercritical fluid extraction. Extraction efficiency for all these methods solely depends on the sample and solvent matrix [11].

Mechanical shaking is quite easy and suitable for petroleum hydrocarbon extraction from various environmental samples [65, 66]. It involves shaking the sample with a solvent. Desiccant (e.g., Na_2SO_4) is sometimes added to remove humidity and facilitate the breaking of the sample, thereby increasing its surface area for excellent contact with the extracting solvent. However, it is not an approved standard method by the USEPA because its efficiency depends on the type of sample [11]. Soxhlet extraction (EPA Method SW-846 3540) is the most commonly used and it is quite efficient for the extraction of the semivolatiles. It involves heating and refluxing of the sample with a solvent continuously for a long period of time (16–48 hours or more) but generates a large volume of extract for concentration and it is less appropriate for the volatiles [67, 68].

Ultrasonic extraction (EPA Method SW-846 3550) method is also very appropriate for the semivolatiles. It uses sound waves (ultrasonic vibrations) to enhance the transfer of the desired compounds from the sample to the solvent. It is a faster method than Soxhlet extraction and requires a relatively lesser amount of solvent [11]. However, it is labor-intensive in that it requires multiple extractions, decanting, and filtration for every sample processed. Accelerated solvent extraction (ASE) is another method for the extraction of semivolatile organic compounds. It is otherwise referred to as subcritical fluid extraction and has reportedly met the requirements for EPA Method 3545 (pressurized fluid extraction) in that it has wider coverage in its application and a good extraction efficiency equivalent to Soxhlet extraction method [67].

ASE uses organic solvents like dichloromethane for its operation. The solvent is heated and pressurized, before being passed through the sample for quick and efficient removal of the desired compounds from the sample matrix [11, 67]. The method requires a shorter extraction period and smaller volume of solvent compared to the conventional methods and, thus, it is a good alternative to both Soxhlet and ultrasonic extraction [23, 68]. However, it is an expensive technique and

has the tendency of extracting many interferences together with the desired analytes because of the high temperature it uses for its operation. Therefore, column cleanup may be required after the extraction process before the analytical determination. Moreover, the extraction process is though shorter compared to Soxhlet extraction method but the preparation time for the extraction cells is long and rinsing consumes a lot of solvent [68, 69].

Supercritical fluid extraction (SFE) is a standard EPA method for total recoverable petroleum hydrocarbons (3540) and polycyclic aromatic hydrocarbons (3561). It involves heating and pressuring of the mobile phase (e.g., CO_2) to supercritical levels, whereby it possesses the properties of both gas and liquid (supercritical fluid). The fluid is then passed through the sample for the concentration of the analytes on a particular sorbent, after which they are eluted with a solvent and analyzed conventionally [11].

5.4. Column Cleanup and Separation. Column cleanup is a process used to separate organic analytes from their interfering compounds of different polarity which were possibly coextracted along with the analytes [70]. It is a very important aspect of infrared-based and gravimetric methods because they are very sensitive to nonpetroleum interferences. It is however not commonly utilized in gas chromatography-based methods because the presence of interfering compounds is not difficult to identify by experienced analysts [11].

Such interferences include the following:

- (i) Natural organics that are not related to petroleum, for example, animal and vegetable derived hydrocarbons.
- (ii) Oxygenated metabolites from biodegraded petroleum origin, for example, organic acids, alcohols, ketones, aldehydes, and phenols.
- (iii) Artifacts from laboratory or sampling equipment, for example, phthalates.
- (iv) Non-petroleum-related chemicals, for example, pesticides and chlorinated solvents [70].

In the infrared-based and gravimetric category, a small quantity of silica gel is added to the extract vial and shaken to remove the polar compounds before the analysis whereas, in the GC methods, the adsorbent (e.g., silica gel) is packed into a glass column. The sample extract is then run through the column which retains the polar substances while the compounds of interest are eluted with an appropriate solvent. This is followed by reconcentration of the eluates and analysis [70]. Aside from the cleaning of the extract, silica gel column also fractionates the petroleum hydrocarbon extract into aliphatic and aromatic fractions for separate determination [13, 48].

6. Analytical Procedures for TPHC in Water and Sediments

There are many conventional analytical methods available for the measurement of TPHC concentrations in various environmental samples. Some are more applicable for field

screening while others are suitable for laboratory uses [11, 13, 71]. The most commonly used include infrared (IR) spectroscopy (EPA Method 418.1), gravimetry (EPA Method 1664A), gas chromatography with flame ionization detection (GC/FID) (EPA Method 8015), gas chromatography with mass spectrometric detection (GC/MSD) (EPA Methods 8270 and 625), ultraviolet spectrophotometry, immunoassay (IMA) (EPA Methods 4030 and 4035), Raman spectroscopy, and fluorescence spectroscopy [8, 52, 72, 73]. Liquid samples are mostly prepared for analytical determination by liquid-liquid extraction (LLE) or solid phase extraction (SPE) while solid samples are commonly made ready by Soxhlet extraction method [74]. This section will therefore present the strengths and weaknesses of some of the methods.

6.1. Gravimetric Method. There are basically two gravimetric EPA methods. These include EPA 413.1 for oil and grease and EPA 1664A for silica gel n-hexane extractable material (also regarded as total petroleum hydrocarbons). They both involve solvent extraction, evaporation, and weighing to a constant weight [52] but the oil and grease method does not differentiate the polar organic matter from the petroleum hydrocarbon portion [74]. EPA 1664A was developed to replace EPA 413.1 that uses Freon 113 (a Class I ozone-depleting substance) as its extracting solvent. The new method performs extraction with n-hexane which is more environmentally friendly but flammable and could determine total petroleum hydrocarbon concentration in the same procedure for the oil and grease analysis [75].

EPA 1664A procedure begins with adjustment of the aqueous sample pH to a value less than 2 with either H_2SO_4 or HCl. The sample is then extracted with n-hexane using LLE (or SPE) method and the organic portion is filtered through a funnel containing anhydrous Na_2SO_4 , after which the solvent is distilled off from the flask at $85^\circ C$ in a water bath. The flask is then dried and weighed to constant weight for the estimation of the oil and grease concentration [75]. For the TPHC determination, the oil and grease in the flask is dissolved in fresh portion of n-hexane. A suitable amount of silica gel is added to remove the polar substances (e.g., fats, dyes, oils, waxes, and some heavier organic molecules from animals and plants origin) in the extract and the mixture is stirred using a magnetic stirrer, filtered, and gravimetrically determined as nonpolar material (NPM), also known as silica gel treated n-hexane extractable material (SGT-HEM) [74, 76].

Solid samples (sludge, soil, and sediment) are catered for in the EPA SW-846 Test Method 9071B in which a wet sample is to be acidified with concentrated HCl. Acidified sludge sample is dried with either anhydrous sodium sulphate or magnesium sulphate and soil or sediment sample with sodium sulphate prior to the Soxhlet extraction with n-hexane. The NPM and SGT-HEM in the sample are thereafter gravimetrically determined as earlier described in the EPA 1664 procedures [77]. Other gravimetric methods reported for solid samples involved the addition of 3 g KOH (to enhance the extraction of the humic substances) and 100 cm³ methanol to about 100 g air-dried samples prior to the Soxhlet

extraction process. The subsequent steps involving gravimetric measurement of the polar and nonpolar compounds are as discussed above [78–80].

Gravimetric determination of TPHC in environmental samples is quite simple and affordable and has thereby gained a very huge patronage over the years because it does not require any special equipment. However, it is more applicable to samples with high concentration of analytes because of its low sensitivity. It is time-consuming, especially at the solvent evaporation stage, and has great tendency of losing the low-molecular-weight compounds, thereby introducing errors into the measurement [58, 73]. The extraction efficiency of the solvent is relatively low for the higher-molecular-weight compounds but can be reasonably enhanced with the addition of salt (sodium chloride). The coextraction of some organic matter with many polar functional groups is also encouraged by the low polarity of the solvent [81, 82].

6.2. Infrared Spectrophotometry. Similarly, two infrared (IR) based methods are in use for petroleum hydrocarbon related measurements. They include EPA 413.2 for total recoverable oil and grease (TOG) and EPA 418.1 for total recoverable petroleum hydrocarbons (TRPHCs) [13]. The oil and grease method is limited in application unlike EPA 418.1 or the modified EPA 801.5 which was widely accepted as a standard method for the assessment of hydrocarbon levels in the petroleum contaminated sites [13, 46]. The method is capable of determining different classes of hydrocarbon as either oil and grease (OG), gasoline range organics (GRO), or total petroleum hydrocarbons (TPHCs) [46]. It uses light absorption of the CH_2 bond at 2930 cm^{-1} which is characteristic of the oil and grease for its measurement [58].

EPA 418.1 involves acidification of the water sample to $pH < 2$, extraction of the analytes from the sample matrix using 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) or tetrachloromethane (CCl_4), and filtration of the extract through anhydrous sodium sulphate for moisture removal. The filtered extract is then made up to 100 mL with the extraction solvent and then stirred with a sufficient quantity of silica gel for the removal of the fatty matter before the absorbance measurement from 3200 cm^{-1} to 2700 cm^{-1} . The final reading is then compared with the absorbance of a reference oil standard [13, 75]. The advantages of the method include elimination of the solvent evaporation step, making it more appropriate for the volatile components of petroleum [58, 79]. The measurement is very reproducible and more accurate, saves time, and is relatively easier [82]. Generally, IR methods give higher results than gravimetric methods, possibly because of the loss of volatile components due to the evaporation step in the latter [58].

However, IR readings sometimes may not suggest petroleum contamination in water or sediment sample because some compounds from nonpetroleum origin (e.g., humic or fulvic acid) may generate strong absorbance in the infrared range, yielding a false positive result especially when the cleanup step is omitted [52, 59]. It is also limited in its application as no adequate information is provided on the type of hydrocarbon present. The halogenated solvents (Freon, CCl_4) used for extraction in this method

are though relatively nontoxic and nonflammable but are primary sources of ozone-layer-depleting substances which were required to be phased out in the Clean Air Act Amendments of 1990 [46]. EPA 418.1 is therefore being gradually replaced with EPA gravimetric (EPA 1664) and/or gas chromatographic (e.g., ISO 9377-2 or 8015D) method [52, 76, 82].

6.3. Gas Chromatography. The revised EPA 8015D called “Non-Halogenated Organics Using GC/FID” was specifically developed to take care of volatile and semivolatile organics separately as gasoline range organics (GRO) in the boiling point range of 60°C–170°C (C6–C10) and diesel range organics (DRO) in range of 170°C–430°C (C10 to C28). The method has the ability to provide some necessary information on the product type unlike the gravimetric and IR methods [13]. The volatile samples are usually introduced into the gas chromatograph (GC) by purge and trap method (EPA 5030 for aqueous or EPA 5035 for solid sample) [52, 83].

Aqueous semivolatile samples are mostly prepared by liquid-liquid extraction (EPA 3510) technique, although solid phase extraction (EPA 3535) may as well be used. Solid samples are usually extracted with Soxhlet device (EPA 3540). The extracts are subjected to either alumina (EPA 3611) or silica gel (EPA 3630) column cleanup with which the fatty matter is removed on the basis of polarity and petroleum hydrocarbons are fractionated into aliphatic and aromatic fractions. Each fraction is then injected directly into a gas chromatograph equipped with a nonpolar capillary column for analytical determination [11, 83]. Identification of analytes is done by comparing the retention time of an individual compound to that of a reference standard. Calibration standards are used to prepare calibration curves with which the compounds of interest are quantified [11].

The aliphatic and aromatic fractions are analyzed separately on the gas chromatograph using a flame ionization detector (GC-FID) which is mostly preferred for its relative sensitivity and selectivity for hydrocarbons. The two fractions are usually divided into carbon number ranges (GRO and DRO) on the basis of the PAH and n-alkane markers, respectively [52, 84]. The areas covered by the resolved and unresolved (UCM) components are most commonly estimated to determine the total petroleum hydrocarbon (TPHC) level in the sample [84–86]. Unfractionated extract can also be quantified as the oil and grease, yielding a concentration greater than the sum of the aliphatic and aromatic fractions [84].

Total hydrocarbons are sometimes measured with FID while the aromatic fraction is determined with a photoionization detector (PID). The aliphatic fraction is therefore estimated by subtracting the aromatic from the total hydrocarbon result. However, PID is not entirely selective for aromatic compounds and therefore can overestimate [13]. Alternatively, GC coupled with mass spectrometric detector (MSD), especially in the selected ion monitoring (SIM) mode, can produce a better result in the analysis of aromatic compounds. This is because it has the capacity to detect a compound present at an extremely low concentration in a complex matrix, provided that the desired compound

has a prominent fragment ion at a mass that differentiates it from other hydrocarbon compounds and can also offer more comprehensive information about the identity of the compound [52, 72].

With GC methods, the identity of the fresh to mildly degraded oil can be unraveled in the environmental samples for pattern recognition [86]. The profile of unresolved complex mixtures (UCM) in the contaminated samples can be adequately characterized and resolved [87]. But the cost of analysis, operational time required, and sample matrix effects may be higher [88]. Overlap of carbon number ranges could be another challenge because a section of the GRO may be reported as DRO and vice versa [13, 52].

6.4. Ultraviolet Fluorescence Spectrophotometry. Ultraviolet fluorescence (UVF) spectrophotometry is a fast and valuable screening method for TPHC analysis in the environmental samples. It involves solvent extraction and optical measurement of the hydrocarbon molecules using an ultraviolet fluorescence spectrometer. It is always used in the field for aqueous samples without solvent extraction [58, 74, 89]. The aromatic hydrocarbons fluoresce when their π -bonds are excited by ultraviolet light and the hydrocarbon concentration in the sample extracts is measured using a fluorometer [74]. The technique has greater potential to distinguish low-molecular-weight aromatic hydrocarbons with 2 to 3 rings from the high-molecular-weight compounds [11, 58]. North Carolina in the United States has recently approved the method for monitoring spillage from leaking underground storage tanks as a replacement for the GC/FID (EPA 8015D) method [90]. However, aliphatic alkanes do not respond to ultraviolet radiation because they do not have π -bonds. Therefore, samples containing paraffinic oil cannot be detected by this method [74].

For reliable analytical results, a calibration curve must be prepared using specific hydrocarbon contaminants. Analytical recovery of UVF was reportedly good with n-hexane (132%) as an extraction solvent compared with methanol (40%) [74] but the accuracy and reproducibility at a low concentration range were found to be relatively low [82]. It is not a suitable method for fingerprint analysis because nonhydrocarbon compounds can also emit at the same wavelength as the analytes, thus causing interference [89].

7. Levels of Total Petroleum Hydrocarbons in the Environment

The total petroleum hydrocarbon results published from different countries across the world are presented in Tables 1 and 2. The levels reported in water matrix ranged from “not detected” (ND) to 260,000 $\mu\text{g/L}$. The highest values (60,000–260,000 $\mu\text{g/L}$) were recorded in the Deepwater Horizon, Gulf of Mexico [91], while the lowest values (0.05–4.13 $\mu\text{g/L}$) were found in the Gulf of Thailand and East Coast of Peninsular Malaysia [6]. The first world immense accidental blowout occurred in June 1979 at the Ixtoc-I most productive oil well in the Gulf of Mexico where more than 3.4 million barrels were spilled [92]. This might be responsible for the higher level of TPHC measured from the

TABLE 1: Levels of TPHC in water samples around the world ($\mu\text{g/L}$).

Sample source	Concentrations reported	Analytical method	References
<i>Africa</i>			
Groundwater samples collected in some communities in Rivers State, Nigeria	33,076 (max)	GC/FID	[63]
Ubeji surface water, Warri, Nigeria	73,500	Gravimetry	[96]
Surface water from the vicinity of Nigerian National Petroleum Corporations (NNPC) Oil Depot in Apata, Ibadan Metropolis, Nigeria	20,340–27,400	Gravimetry	[110]
Groundwater in communities in Niger Delta region of Nigeria	1,352–12,110	GC-FID	[111]
<i>Asia</i>			
Strait of Johor, in Peninsular Malaysia	25–2,795	—	[112]
Bohai Bay, China	24–508	—	[109]
Main Outfall Drain in Al-Nassiriya City, Southern Iraq	0.01–8.76	UVF	[113]
Setiu Wetlands, Terengganu, Malaysia	4–121	UVF	[114]
Coastal waters from Malaysian west coast	5–386	—	[112]
Dungun River basin water, Malaysia	12–41	UVF	[50]
Gulf of Thailand and East Coast of Peninsular Malaysia	0.05–4.13	UVF	[6]
Levantine Basin, Israeli Coastline	19–88	—	[115]
Northwestern Arabian Gulf	1.2–546	—	[116]
<i>America</i>			
Jamaica Bay, New York Metropolitan Area	10–20	GC/FID, UVF & GC/MS	[117]
Deepwater Horizon, Gulf of Mexico	60,000–260,000	—	[91]
Ixtoc-I Blowout, Gulf of Mexico	5–106,000	—	[93]
<i>Europe</i>			
Seawater of North Cape (Norway)	483 (mean)	GC/MS	[72]
Romanian Black Sea Sector	29–271	UVF	[118]
Kara Sea	8–408	—	[119]
Pechora Sea	2–87	—	[120]
<i>Australia</i>			
Yellow Water, Kakadu National Park	ND–200	GC/FID	[121]

site some years later [93]. Another spill in the region from an oil well in the Deepwater Horizon popularly referred to as “the worst environmental disaster in the history of the US” claimed not less than 11 lives in April 2010. About 4.2 million barrels were reportedly spilled in the ugly incidence that lasted for about 87 days in which British Petroleum (BP) was implicated, hence the reason for higher TPHC level in the study conducted at the site about three years later [91, 94].

The European Union’s target value for TPHC in estuary and harbor water is $300 \mu\text{g/L}$. This value was greatly exceeded in many water bodies across the world, signifying anthropogenic input of hydrocarbons into the environments [95]. With reference to the collated data as shown in Table 1, TPHC levels were exceptionally higher in the Gulf of Mexico and the Niger Delta region of Nigeria, where petroleum exploration activities are being undertaken, than in other regions [63, 91, 93, 96].

Table 2 showed that the TPHC levels in the sediment samples analyzed across the world varied from ND (not detected)

to $16,500 \text{ mg/kg}$. The lowest values (ND– 1.71 mg/kg) were recorded from the coastline and mangroves of the Northern Persian Gulf [97] and the highest ones (300 – $16,500 \text{ mg/kg}$) were recorded from the Pearl River Estuary, China [98]. The minimum value of 10 mg/kg stipulated by the United Nations Environment Programme was exceeded in most countries, suggesting increasing petroleum hydrocarbon pollution in the fresh and marine aquatic environments across the globe. Urban-industrial activities can increase the concentration to between 10 and $1,000 \text{ mg/kg}$ while levels $>3,000 \text{ mg/kg}$ will usually be found in oil spill sites [4, 99, 100]. This indicates a greater influence of industrial activities as well as oil spillage on the petroleum hydrocarbon levels in most of the coastal sediments all over the world. The levels were extremely higher in some estuaries in China [56, 98, 101–103], Ceuta Harbor in North Africa [104], São Gonçalo Channel in Pelotas, Rio Grande do Sul, Brazil [22], and Clyde Estuary, United Kingdom [105]. TPHC was generally much higher in the sediment than in the water column.

TABLE 2: Levels of TPHC in sediment samples around the world (mg/kg).

Sample source	Concentrations reported	Analytical method	References
<i>Africa</i>			
Ceuta Harbor, North Africa	496–6,972	Gravimetry	[104]
Soil in communities in Niger Delta region of Nigeria	1,242–5,200	GC-FID	[111]
Bizerte Lagoon, Tunisia	0.05–20	—	[122, 123]
<i>Asia</i>			
Arabian Gulf	444 (mean)	UVF	[124]
Bohai Bay, China	6.3–535	UVF	[125]
Arabian Gulf sediment, Kuwait	50–1,122	UVF	[78]
Musa Bay sediments	17–97	UVF & GC/MS	[126]
Khawr-e Musa Bay	18–89	UVF & GC/MS	[127]
Coastal Area of Putatan and Papar, Sabah	0.26–4.59	UV/VIS	[128]
Main Outfall Drain in Al-Nassiriya City, Southern Iraq	0.09–5.70	UVF	[113]
Coastline and mangroves of the Northern Persian Gulf	ND–1.71	UVF	[97]
Southeast Coast of India	2.2–5.6	UVF	[8]
Koh Sichang-Sriracha, Thailand	1.1–153.4	UVF	[99]
Saudi Arabia	62–1,400		[129]
Changjiang Estuary, China	2,200–11,820	—	[56, 101]
Pearl River Estuary, China	300–16,500	—	[98, 102, 103]
<i>America</i>			
São Gonçalo Channel, Pelotas, Rio Grande do Sul, Brazil	177–5,893	Gravimetry/GC/MS	[22]
Barnegat-Bay-Little Egg Harbor Estuary, USA	47–1,003	Iatroscan Mk6s/FID	[130]
Galveston Bay, USA	4.2–1,814	—	[131, 132]
Todos os Santos Bay, Brazil	1.6–11	GC/MS	[133]
Trinidad Coast	3.0–1,824	UVF	[134]
<i>Europe</i>			
Clyde Estuary, UK	34–4,386	Iatroscan Mk6s/FID	[105]

General assessment of the analytical methods employed by researchers for the determination of total petroleum hydrocarbons in both water and sediment matrices as shown in Tables 1 and 2 revealed greater use of UVF which was quicker and easier than other existing methods [106]. Although the equipment is mostly available as a portable field device, any data obtained should often be validated with off-site laboratory equipment for better quality and reliability [107]. The IR method (EPA 418.1) is gradually fading away because of the mandated halogenated solvents which are environmentally unfriendly, as gas chromatographic and gravimetric (EPA 1664) procedures are now increasing in patronage [108]. Total petroleum hydrocarbon is more determined in the Asian environment than in other continents of the world probably because of the great abundance of crude oil in many countries in the region. It is very obvious that spillage of oil, industrial effluent discharge, and urban runoff are the major reasons for higher TPHC levels in marine environment and therefore steps should be taken to minimize these to the barest minimum across the globe [109].

8. Conclusion

Although solid phase extraction has a better extraction efficiency than LLE, its application in the petroleum hydrocarbon extraction from the water matrix is limited because it is yet to be validated by the United States Environmental Protection Agency for this particular analysis. Therefore, LLE remains the most commonly used method because of its affordability, simplicity, and relative efficiency. Similarly, the solid samples are more commonly extracted with Soxhlet extractor which is time-consuming compared to the accelerated solvent extraction because it is easy to use and quite cheaper. Aliphatic hydrocarbons which are the primary components of petroleum hydrocarbons are mostly more determined in the marine sediment than in the water column because they have relatively low solubility in water and thereby concentrate in the bottom sediment.

Many analytical methods are available for the TPHC measurement in the environmental samples. Some measure TPHC on the basis of the aliphatic or aromatic fraction alone while few others combine the two fractions for the

measurement. The results taken using different methods are therefore in most cases incomparable owing to their different background. However, off-site laboratory equipment is more preferred for the analytical determination of the analytes than the portable field devices because it generates good data which are much more reliable. The TPHC concentrations were found to be extremely higher in the spillage sites and greatly industrialized areas. Hence, there is a greater need for compliance with environmental laws as regards the oil exploration and transportation, as well as waste discharge into the marine environment in order to ensure safety of aquatic and human lives.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

References

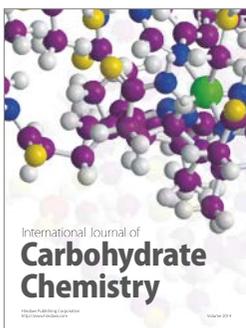
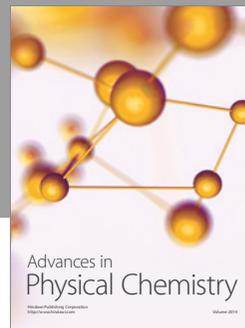
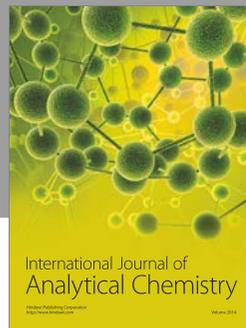
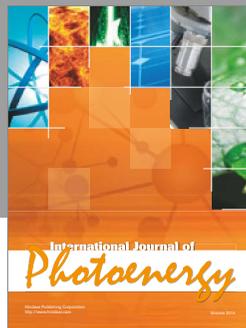
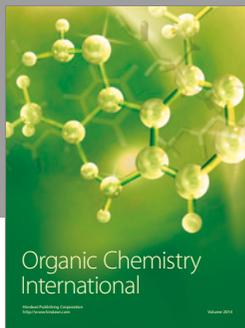
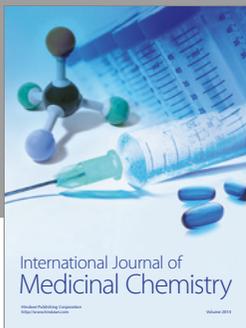
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