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A comparison study of gravimetric and ultraviolet fluorescence methods for the analysis of total petroleum hydrocarbons in surface water

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**A COMPARISON STUDY OF GRAVIMETRIC AND
ULTRAVIOLET FLUORESCENCE METHODS FOR THE
ANALYSIS OF TOTAL PETROLEUM HYDROCARBONS IN
SURFACE WATER**

A Thesis Presented

by

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Abstract

Petroleum hydrocarbons are important environmental contaminants and determination of petroleum-derived hydrocarbons are significant. The definition of total petroleum hydrocarbons depends on the analytical method used as no single method detects the entire range of petroleum-derived hydrocarbons. Two analytical methods have been used in this study for the analysis of aqueous samples for total petroleum hydrocarbons. EPA has approved Method 1664A as a standard testing procedure for the analysis of Total Petroleum Hydrocarbons in water. This study compares the EPA Method 1664A and Ultraviolet Fluorescence Technology for the analysis of total petroleum hydrocarbons in aqueous matrix. The study compared the results of the analysis of surface water samples and artificial samples made from 1,2 diphenylbenzene (o-terphenyl) and stearic acid, o-terphenyl, 1,4 diphenylbenzene (p-terphenyl), Formula Shell 10W-30 Motor Oil and No.6 Fuel Oil. The results are found to be comparable for the surface water samples over the reportable range of both the analytical methods. It is observed that the o-terphenyl standards show weak fluorescence at low concentrations and the light emission property decreases with increase of concentration at the wavelength used in the fluorometer. The Formula Shell 10W-30 Motor oil has shown a feeble response towards the ultraviolet excitation of the samples in inert solvents. Ultraviolet excitation of No.6 fuel oil and p-terphenyl has recorded 5 and 100 times fluorescence on comparison with the TPH-Oil calibration standards. As the optical experiments indicate that the fluorescence property of hydrocarbons and oils vary significantly, standards used for calibrating the instrument should be site and type specific.

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1 Introduction

Petroleum and its products dominate as one of the important commodities consumed in the modern world. Petroleum is the term used to describe naturally occurring hydrocarbon-rich fluids that have accumulated in subterranean reservoirs. Petroleum products are a complex mixture of hydrocarbons composed mainly of carbon and hydrogen in different molecular arrangements. According to a 1990-1999 survey by National Research Council, 35% of the petroleum contamination in North American waters happens due to oil-well accidents, spills from tankers, leaks from underground storage tanks, pipelines, run-off from petroleum distribution facilities and transfer operations.

Analytical methods are used to detect and assess the severity of contamination in natural and wastewaters, and analytical data are a prerequisite for permit application and compliance monitoring. They are used to support decision making regarding the regulatory, scientific and economical issues at an impacted site or water body. Generally, analytical methods describe collection, preservation and storage of samples, procedures to concentrate, separate, identify and quantify the contaminants in the sample, quality control criteria the analytical data should meet and the reporting of analytical data.

The objective of this study is to evaluate the agreement of EPA Method 1664A and Ultraviolet Technology for the analysis of total petroleum hydrocarbons in aqueous samples for site characterization. The comparison study of analytical methods determines the data usability of a non-standard or less rigorous technique against a standard laboratory method. EPA Method 1664A is approved as the standard method for the determination of total petroleum hydrocarbons. The ultraviolet fluorescence technology

designed for field deployment has generated interest due to its commercial availability, reduced costs and turnaround time for sample analysis and easier and safer technology. The initial effort of the study is to establish a detection limit, precision bias or quality assurance of the data obtained using EPA method. The main course of the study is to analyze artificial samples prepared from o-terphenyl, stearic acid, p-terphenyl, Formula Shell 10W-30 Motor oil and No.6 fuel oil and natural surface water samples and to compare the data obtained from two different base technologies for the determination of total petroleum hydrocarbons.

2 Literature Review

Total Petroleum Hydrocarbons are large family of several hundred petroleum based chemical compounds that are present in crude oil and comprise of refinery gas, liquefied petroleum gas (LPG), naphtha, gasoline, aviation fuel, marine fuel, kerosene, diesel fuel, distillate fuel oil, residual fuel oil, mineral oil, lubricants, white oil, grease, wax as well as asphalt. The relative proportion of different hydrocarbons in the crude oil is highly variable. Hydrocarbons include alkanes, cycloalkanes, aromatic hydrocarbons and heteroatom-containing (nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium) constituents (Speight, 1999). The exact molecular composition of petroleum varies widely and it is dictated by the processes by which the petroleum was formed, the local and regional variations in temperature and pressure to which the precursors were subjected as well as age and depth of oil field (Gruse and Stevens, 1960). The proportions of elemental compositions vary over fairly narrow range as shown in Table 2.1.

Table 2.1 Elemental composition in petroleum by weight percentage (The Chemistry and Technology of Petroleum; 1999, J.G. Speight)

<i>Element</i>	<i>Weight Percentage</i>
Carbon	83.0- 87.0%
Hydrogen	10.0- 14.0%
Nitrogen	0.1- 2.0%
Oxygen	0.05- 1.5%
Sulfur	0.05- 6.0%
Metals (Ni and V)	<1000 ppm

2.1 Hydrocarbon Components

Naturally occurring hydrocarbons are major contributors to the composition of petroleum (Bestougeff, 1967; Hobson and Pohl, 1973). The hydrocarbon components of petroleum can be divided into three classes:

1. Paraffins: Include saturated hydrocarbons with straight or branched chains, but without ring structure (Speight, 1999). They contain only carbon and hydrogen molecules with a general formula of C_nH_{2n+2} . Paraffins form the predominant fraction of any particular crude oil (Rossini and Mair, 1959). Generally they contain 5 to 40 carbon atoms per molecule even though shorter and longer molecules may also be present in the mixture. Slightly branched paraffins predominate over the highly branched materials (Speight, 1999). The proportion of paraffinic hydrocarbons in petroleum usually decreases with increasing molecular weight or boiling point. But, iso-paraffins occur throughout the boiling range of the petroleum fractions (Speight, 1999). The alkanes, propane (C_3H_8) and butanes (C_4H_{10}) or mixtures of both form the major constituents of *liquefied petroleum gas* (LPG). The hydrocarbons from pentane (C_5H_{12}) to nonane (C_9H_{18}) are refined into gasoline, the ones from decane ($C_{10}H_{20}$) to hexadecane ($C_{16}H_{34}$) into diesel fuel and kerosene (Altgelt and Boduszynski, 1994). Fuel oil and lubricating oil are produced from C_{16} or higher alkanes up to C_{40} . Waxes (normal paraffins) up to C_{36} carbon atoms have been isolated from petroleum.
2. Naphthenes (*Cycloparaffins*): Include saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains. They usually contain five- or six-membered rings or their combinations and occur as polycyclic structures. The mono- and bicyclic naphthenes are generally the major types of naphthenes in the lower boiling fractions of petroleum and the presence of alkyl side

chains are observed with increase in boiling point or molecular weight. As the molecular weight of the petroleum fraction increases, there is considerable increase in the amount of naphthenic species. Occurrence of condensed naphthenic ring systems and alkyl-substituted naphthene ring system increases with increase in molecular weight of the fractions (Speight, 1999).

3. Aromatics: Include hydrocarbons containing one or more aromatic nuclei. Majority of aromatics contain paraffinic chains, naphthene rings, and aromatic rings side by side. However, aromatic hydrocarbons without the accompanying naphthene rings or alkyl-substituted derivatives are present in appreciable amounts only in lower petroleum fractions. There is a general increase in proportion of aromatic hydrocarbon species with increasing molecular weight or higher boiling fractions (Speight, 1999).

There exists a relationship between these various hydrocarbon constituents of crude oil which is shown by Figure 2.1. These inter-conversion schemes during the formation, maturation and *in-situ* alteration of petroleum occur due to addition or loss of hydrogen atom.

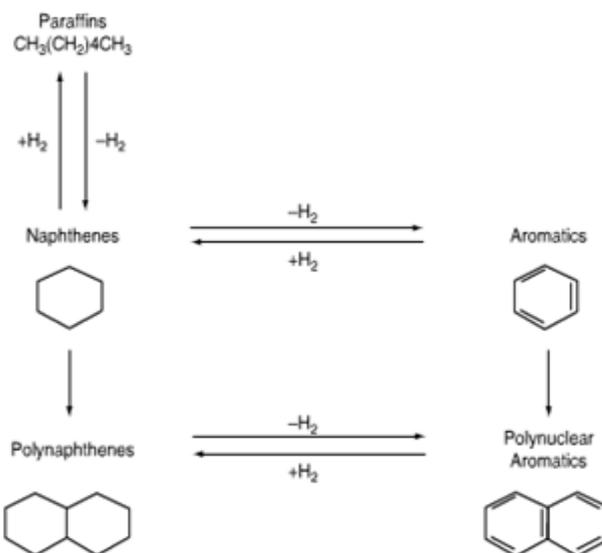


FIGURE 7.2 Interrelationship of the hydrocarbon types in petroleum.

Figure 2.1 Relationship between various hydrocarbon constituents of crude oil (The Chemistry and Technology of Petroleum; 4th Edition, J.G. Speight)

A widely used classification of crude petroleum distinguishes the crude oils on the hydrocarbon base. The division is according to the chemical composition of the 250-300^oC fraction. The petroleum classification according to the hydrocarbon components is shown in the Table 2.2.

Table 2.2 Petroleum Classification according to Chemical Composition (The Chemistry and Technology of Petroleum; 1999, J.G. Speight)

Class of Crude	Composition of 250-300 ^o C fraction				
	% Paraffinic	% Naphthenic	% Aromatic	% Wax	% Asphalt*
Paraffinic	46-61	22-32	12-25	1.5-10	0-6
Paraffinic- naphthenic	42-45	38-39	16-20	1-6	0-6
Naphthenic	15-26	61-76	8-13	Trace	0-6
Paraffinic- naphthenic- aromatic	27-35	36-47	26-33	0.05-1	0-10
Aromatic	0-8	57-78	20-25	0-0.5	0-20

*Asphalt is the major product of petroleum refinery which is made up of the nonvolatile hydrocarbons in the crude oil along with the similar materials produced by thermal alteration during distillation step.

2.2 Analytical Methods for the Determination of Petroleum Hydrocarbons

In the earlier days of the petroleum refining industry, methods for the analysis and characterization of petroleum and petroleum products were developed to satisfy the special needs of refiners with regard to the type of petroleum, yields and properties of fractions, as well as to the nature of the products to be processed. Some types of petroleum have economic advantages as they require less specialized processing than other type of crude oil containing low concentrations of desirable fuel or lubricant constituents. So, evaluation of petroleum to assess the various types of hydrocarbon was inevitable. These methods developed by the refiners were considered proprietary and were not normally available. Consequently, various organizations such as American Society for Testing and Materials (ASTM), Environmental Protection Agency (EPA) developed standard methods for the determination of petroleum hydrocarbons. Wide variety of appropriate analytical methods, as well as development of laboratory instruments and standards has improved the approaches to petroleum hydrocarbon analysis.

The following analytical equipments and standard tests are used for the evaluation of petroleum hydrocarbon in soil or aqueous samples

2.2.1 Spectroscopic Methods

Spectroscopic studies have played an important role not only in the analysis of petroleum hydrocarbons, but also for its characterization and identification. The spectroscopic technique utilizes the interaction between radiation and sample as a function of wavelength (λ). The spectroscopic technique measures quantitative fraction of light that

passes through a given sample. In a spectrophotometer, a light from the lamp is guided through a monochromator, which picks light of one particular wavelength out of the continuous spectrum. This light passes through the sample that is being measured. After passing through the sample, the intensity of the transmitted light is measured with a photo-sensor, and the absorbance for this wavelength is calculated. The concentration of a sample can be analyzed by comparing the absorbance of the sample at the given wavelength to the results of a series of standards. There is a logarithmic relationship between transmittance and the concentration of the absorbing species which is explained by Beer-Lambert law and this law is applied in all the spectroscopic techniques.

Following spectroscopic techniques can be used to study the chemical composition of petroleum.

1. Infrared Spectroscopy: *Infrared* (IR) spectroscopy is a simple procedure which utilizes the absorption of infrared region of the electromagnetic spectrum. The technique exploits the fact that molecules have specific frequencies which causes the changes in the vibrational and rotational energy of the chemical bonds within organic molecules. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures of polynuclear aromatic species (Yen, 1973). Absorption of shorter IR wavelengths can excite vibrational (stretching, rocking, wagging, twisting) changes, while absorption of longer wavelength, lying adjacent to microwave region results in the molecular rotation. The frequency of vibration can be associated with particular bond type. Analyzing the infrared spectrum for a sample provides quick, yet detailed data on the distribution of carbon-hydrogen group, functional groups of

various petroleum constituents (Wen and Yen, 1978), saturated hydrogen-to-saturated carbon ratio, paraffinic and naphthenic character, methyl group content and paraffin chain length. With the invention of the measurement technique *Fourier transform spectroscopy* in which spectra are collected based on measurements of the temporal coherence of a radiative source, using time-domain measurements of the electromagnetic radiation, the entire spectrum was obtained in a fraction of a second. *Fourier transform infrared (FTIR) spectroscopy* lead to increased sensitivity and precision and achieved quantitative estimates of various functional groups of higher molecular weight solid constituents of petroleum and group-type analysis.

2. Nuclear Magnetic Resonance Spectroscopy: *Nuclear magnetic resonance* (NMR) spectroscopy analyzes the quantum mechanical magnetic properties of atomic nuclei to determine different electronic local environments of hydrogen, carbon, or other atoms in an organic compound. The protons and neutrons constituting the elementary particles of nucleus have a quantum mechanical property of spin. A spinning charge generates magnetic field. In the absence of a magnetic field, these are randomly oriented but when an external magnetic field is applied they line up parallel to the applied field, either spin aligned or spin opposed. The more highly populated state is the lower energy spin spin aligned state. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels. In NMR, electromagnetic radiation is used to flip the alignment of nuclear spins from the low energy spin aligned state to the higher energy spin opposed state. The energy required for the spin-flip depends on the magnetic field strength at the nucleus. With no

applied field, there is no energy difference between the spin states, but as the field increases, the separation of energies of the spin states increases and therefore so does the frequency required to cause the spin-flip and this is referred to as resonance. Resonant absorption will occur when electromagnetic radiation of the correct frequency to match this energy difference is applied. It is this resonant absorption that is detected in NMR.

Nuclear Magnetic Resonance methods have been used for the compositional and structural analysis of petroleum fractions and to test the hydrogen content of Light Distillates, Middle Distillates, Gas Oils, and Residuals (ASTM D 4808-01(2006); ASTM D3701; Hasan, Ali and Arab, 1989). *Proton Magnetic Resonance* (PMR) studies along with infrared spectroscopic studies has allowed structural inferences about the polynuclear aromatic systems (Leon, 1987). This technique also differentiates between hydrogen attached next to an aromatic ring and those farther removed from the ring, identifies atoms in single-ring and multi-ring aromatic compounds and those in olefinic locations. Intermolecular interactions might cause errors which can influence the outcome of calculations in PMR. In this regards *Carbon-13 Magnetic Resonance* (CMR) plays a useful role analyzing the carbon distribution types and thereby determining the aromaticity (Snape, Ladner and Bartle, 1979). Thus PMR and CMR spectroscopic techniques offer potential information about the molecular types in the nonvolatile fraction of petroleum.

3. **Mass Spectroscopy:** *Mass spectrometry* (MS) is an analytical technique that identifies the molecular weight and chemical formula of a compound based on the mass-to-charge ratio of charged particles. The physics behind mass spectrometry is that a

charged particle passing through a magnetic field is deflected along a circular path on a radius that is proportional to the mass to charge ratio, m/e . When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons, leaving behind a molecular ion. If the molecular ion is unstable, residual energy from the collision causes it to chemical fragmentation, thereby forming smaller charged particles (ions). The collection of ions is then focused into a beam and accelerated into the magnetic field and deflected along circular paths according to the masses of the ions. By adjusting the magnetic field, the ions can be focused on the detector and recorded. Since the bulk of the ions produced in the mass spectrometer carry a unit positive charge, the value m/e is equivalent to the molecular weight of the fragment.

Mass spectroscopy plays an important role in the identification of the constituents of constituents of petroleum (ASTM D2425-04; ASTM D2650-99; ASTM D2786-91(2006); ASTM D2789-95(2000) e1; ASTM D3239-91(2006)). The principal advantages of mass spectroscopic methods are high reproducibility of qualitative and quantitative analyses, identify unknown compounds, determine the isotopic composition of elements and structure of a compound, quantify the amount of a compound in a sample and the potential for obtaining the data on carbon numbers homologues in complex mixtures. Different mass spectroscopic techniques have been in use for the analysis of petroleum fractions. The standard test methods ASTM D2786-91(2006) and ASTM D3239-91(2006) uses High Ionizing Voltage Mass Spectrometry for the analysis of hydrocarbon types of gas-oil saturates fractions and aromatic types of gas-oil aromatic fractions respectively. For high-molecular-weight

petroleum fractions, the use of non-fragmenting mass spectrometry (NF-MS) method is preferred. Since, it provides molecular weight and the abundance of each compound in a sample reasonably well, it is used for the determination of molecular weight distribution. Among the important non-fragmenting mass spectrometric techniques are *field ionization mass spectrometry* (FIMS), *field desorption mass spectrometry* (FDMS), *chemical ionization mass spectrometry* (CIMS), *low-voltage electron impact spectrometry* (LVEI-MS). All of these are soft ionization techniques designed to generate cold ions of such low excess energy so that they do not undergo fragmentation to greater extent. *Fast atom bombardment mass spectroscopy* (FAB-MS) is for the analysis of polar, high-boiling samples when fragmentation is desired for identification.

4. **Ultraviolet Spectroscopy:** *Ultraviolet* (UV) spectroscopy uses the light in the ultraviolet region of the electromagnetic spectrum to excite the outer electrons causing electronic transition between energy levels that correspond to molecular orbitals of the system. The principle and procedure of ultraviolet spectroscopy is better explained in Section 2.2.3.4. Ultraviolet spectroscopy can distinguish between aromatic compounds with different ring numbers and configurations (Bjorseth, 1983). The standard test methods ASTM D 1840-07 and ASTM D-2269 99(2005) utilizes the ultraviolet spectroscopy for the evaluation of naphthalene hydrocarbons in aviation turbine fuels and white mineral oils respectively.

2.2.2 *Chromatographic Methods*

Chromatographic procedures are referred to as displacement technique which involves passing a mixture dissolved in a mobile phase through an inert stationary phase, which separates the analyte to be measured from other molecules in the mixture and allows it to be isolated. The two major mechanisms at work during a chromatographic separation are displacement and partition. In the simplest procedure, a glass column is packed tightly with powder size dry particles. The center of the column is hollow. The stationary phase is usually a viscous liquid coated on the surface of solid particles which are packed into the column, although the solid particles can also be taken as the stationary phase. The mobile phase is typically a solvent moving through the column which carries the mixture to be separated. This can either be a liquid or a gas, depending on the type of process. As the sample flows through the column, its different components will adsorb to the stationary phase to varying degrees. Those with strong attraction to the stationary phase move more slowly than those with weak attraction. This differential rate of migration of components as the mixture moves over adsorptive materials provides separation. After the sample is flushed or displaced from the stationary phase, the different components will elute from the column at different times. The components with the least affinity for the stationary phase (the most weakly adsorbed) will elute first, while those with the greatest affinity for the stationary phase (the most strongly adsorbed) will elute last. The different components are collected as they emerge from the column. A detector analyzes the emerging stream by measuring a property which is related to concentration and characteristic of chemical composition.

The more common chromatographic procedures used for the identification of the constituents of the petroleum are column chromatography, gas chromatography, gel permeation chromatography, ion-exchange chromatography and high-performance liquid chromatography, which are discussed in more detail.

1. Column Chromatography: Column chromatography is generally used as a refining or purification technique (Gary and Handwerk, 1984). It isolates desired compounds from a mixture. The chromatographic column consists of a vertical glass tube of 1-5 cm in diameter and 20-100cm in length. The stationary phase in column chromatography is a solid adsorbent. The most common stationary phase for column chromatography is silica gel, alumina or diatomaceous earth. The mobile phase is either a pure solvent or a series of increasingly polar solvents. The mixture to be analyzed by column chromatography is applied to the top of the column. The liquid eluent is passed through the column by force of gravity or by the application of air pressure. An equilibrium is established between the solute adsorbed on the adsorbent and the eluting solvent flowing down through the column. The different components in the mixture have different molecular shape, polarity and interactions with the stationary and mobile phases, and they will be carried along with the mobile phase to varying degrees and a separation will be achieved. The individual components and eluent are collected as the solvent drips from the bottom of the column. Small fractions of the eluent are collected sequentially in labeled tubes and the composition of each fraction is analyzed by thin layer chromatography or other spectroscopic techniques.

Column chromatography has helped to characterize the group composition of crude oils and hydrocarbon products. The method can be applied to conventional petroleum, heavy oils, residual, and bitumen with slight changes in the procedure depending on the nature of materials to be analyzed. This traditional analytical procedure is capable of separating crude petroleum into saturate, aromatic, resin, and asphaltene fractions. Also, studies have proved that column chromatographic methods fail to separate nonpolar aromatics from different resin fractions of petroleum (Islas-Flores et.al, 2005).

2. Gas Chromatography: *Gas Chromatography* (GC) makes use of carrier gas, such as helium, nitrogen, argon or carbon dioxide as the mobile phase. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside glass or metal tubing called column. The sample is injected using a micro-syringe into a flash vaporizer port at the head of the column where it is converted into vapors. The sample vaporizes to form a mixture of carrier gas, vaporized solvent and vaporized solutes. The sample is transported through the column by the flow of inert, gaseous mobile phase. It is within the column that separation of the components takes place. The components partition between the carrier gas (the mobile phase) and the high boiling liquid (the stationary phase) within the column. Each components of the mixture will reach the detector at varying times due to differences in the partitioning between mobile and stationary phases. A detector is used to monitor the outlet stream from the column. Generally, components are identified quantitatively as the area of the peak is proportional to the number of molecules generating the signal and

qualitatively by the order in which they elute from the column and by the retention time of the analyte in the column.

Gas chromatography has been used for the determination of saturated compounds and olefins in cracked naphtha, identification of alkylbenzenes, higher-molecular-weight normal paraffins and volatile components in the mixture (Grob, 1995). The procedure has also been used for the characterization of gasoline and naphtha. Due to the molecular characterizing nature of spectrometric techniques, considerable attention has been given to the combined use of gas chromatography and these techniques. The standard test ASTM D5769-98 makes use of Gas Chromatography/ Mass Spectrometry (GC/MS) for the analysis of benzene and toluene and total aromatics in finished gasoline.

3. Gel Permeation Chromatography: *Gel Permeation Chromatography* (GPC) or *Size Exclusion Chromatography* (SEC) is a chromatographic technique in which the separation is based on differences in the size of the sample molecules. A general rule is that compounds that differ by 10% in size can be separated in the same column. The column packing is made from beads of porous gel made by polymerizing or cross-linking styrene in presence of a non solvent for polystyrene. The size of the pores determines the molecular weight range of the compounds that can be separated. An organic solvent is used as a mobile phase. The polymer to be analyzed is introduced at the top of the column and then is eluted with a solvent. The polymer molecules diffuse through the gel at rates depending on their molecular size. Large molecules cannot be accommodated within the gel beads and are washed out of the column sooner. The lowest-molecular-weight molecule that does not enter the gel

pores is called exclusion limit. Slightly smaller molecules can enter some pores, and so take longer to elute, and small molecules can be delayed further. As they emerge from the bottom of the column they are detected by a differential refractometer from which a molecular size distribution curve is plotted.

In theory, gel permeation chromatography is an attractive technique for the determination of the number average molecular weight distribution of heavier petroleum fractions (Altgelt, 1979; Hausler and Carlson, 1985). But, petroleum samples are not homologous mixtures differing only in molecular weight. It contains constituents widely differing in polarity which can interact with the gel surface to different extent. So a linear relationship between the logarithm of average molecular weight against elution volume may not be expected for a matrix of different hydrocarbons. The lack of realistic standards of known average molecular weight distribution and of similar chemical nature of petroleum constituents for calibration may be a concern.

4. **Ion-Exchange Chromatography:** Ion-Exchange Chromatography is an ion exchange process in which the desired ions are exchanged in sequence and are eluted from the column. Ion-exchange chromatography is widely used in the analyses of petroleum fractions for the isolation and preliminary separation of acid and basic components. There are two types of ion-exchange chromatographic techniques. In cation exchange chromatography, positively charged molecules are attracted to a negatively charged stationary phase. Conversely, in anion exchange chromatography, negatively charged molecules are attracted to a positively charged stationary phase. Ion exchange stationary phases are obtained by cross-linking polystyrene polymer beads of an

appropriate size with varying amounts of divinylbenzene. These materials are called ion exchange media. The size of the species that can diffuse to reach the exchange site is determined by the intermolecular spacing between the polymeric chains of three-dimensional polyelectrolyte resin. To optimize binding of all charged molecules, the acids are extracted from the anion-exchange resins with a benzene-formic acid azeotrope and the bases from the cation exchange resin with a mixture of benzene and propylamine solution. To separate organic acids, it is the negatively charged acid ions that need to be selectively retained. It follows that the stationary phase must contain immobilized positively charged cations as counter ions to interact with the acid ions to retain them. Conversely, to separate cations, the stationary phase must contain immobilized anions as counter ions with which the cations can interact. They are identified on the basis of retention time as compared to standards.

This technique helps in the analysis of acidic and basic hydrocarbon concentrates in petroleum. Isolation and identification of nitrogen compounds from petroleum were done using sodium aminoethoxide in ethanolamine and 72% perchloric acid eluents (Drushel and Sommers, 1966).

5. High-Performance Liquid Chromatography: *High-performance liquid chromatography* (HPLC) is basically a highly improved form of column chromatography. Instead of a solvent being allowed to drip through a column under gravity, it is forced through under high pressures of up to 400 atmospheres. There are two variants in use in HPLC depending on the relative polarity of the solvent and the stationary phase. *Normal phase mode* has found great utility in separating different hydrocarbon types and identifying specific constituent types. This is essentially just

the same as column chromatography. The column is filled with tiny silica particles, and the common solvents are hexane, methanol, water and acetonitrile. A typical column has an internal diameter of 4.6 mm or lesser and a length of 150 to 250 mm. Polar compounds in the mixture being passed through the column will stick longer to the polar silica than non-polar compounds. The non-polar ones will therefore pass more quickly through the column. After the components are partitioned, they pass through the detector. The ideal detector for hydrocarbon group type of analysis is one that is sensitive to hydrocarbons but response should be independent of carbon number. The HPLC detector most often used in petroleum environmental analysis is the fluorescence detector. HPLC methods using fluorescence detection will measure any compounds that elute in the appropriate retention time range and which fluoresce at the targeted emission wavelength. These detectors are particularly sensitive to aromatic molecules, especially the poly aromatic hydrocarbons (PAHs). A UV detector may be used to measure compound like acenaphthylene which do not fluoresce.

HPLC technique is of more important for the identification of molecular types in non-volatile petroleum fractions (Schwartz and Brownlee, 1986; Sharrif et al, 1998). EPA Method 8310 target PAHs but also derived aromatics, such as alkylaromatics, phenols, anilines, and heterocyclic aromatic compounds containing the pyrrole (indole, carbazole), pyridine (quinoline, acridine), furan (benzofuran, naphthofuran), and thiophene (benzothiophene, naphthothiophene) structures. In petroleum samples, alkyl PAHs are strong interfering compounds.

2.2.3 Methods for Petroleum Hydrocarbon Analysis

2.2.3.1 Standard Method 5520

Oil and grease has two primary constituents: fatty matter (typically fats, oils, waxes, dyes, some heavier organic molecules) from animals and plants and hydrocarbons of petroleum origin. Analysis of oil and grease does not distinguish these two major components, but quantifies a group of compounds that have similar solubility in an organic solvent. For liquid samples, four extraction procedures for oil and grease are presented: Liquid-liquid partition gravimetric method (5520 B), Soxhlet method (5520 D), and Solid-phase partition-gravimetric method (5520 G). Each extraction process is described briefly.

1. Liquid-liquid, partition-gravimetric method (5520 B): In this extraction procedure, the sample is first acidified to pH less than 2 using 1:1H₂SO₄ or 1:1HCl. The sample is poured into a separatory funnel and is extracted with 30mL of n-hexane by shaking vigorously for two minutes. When the layers separate, the lower aqueous layer is drained to the original container and solvent layer is drained through a funnel containing a filter paper and 10g sodium sulfate into a distilling flask containing boiling chips. The sample is extracted twice more using 30mL of solvent and the solvent extract is collected in the distilling flask. The flask is fitted with a distillation adapter equipped with a drip tip for the maximum solvent recovery. The solvent is distilled from the flask in a water bath at 85⁰C and the solvent is collected in an ice bath cooled receiver. When visible solvent condensation stops, the bent distillation adapter is replaced with vacuum air adapter connected to vacuum source. Vacuum is applied for one minute to draw air and the flask is removed from the water bath. The flask is wiped to remove moisture and dried in a desiccator.

2. Soxhlet Extraction Method (5520 D): IL sample is acidified to pH less than 2 with 1:1H₂SO₄ or 1:1HCl. Soluble metallic soaps are hydrolyzed by acidification. A filter consisting of muslin cloth disk overlaid with filter paper is prepared and washed with 100mL distilled water using vacuum. Then, the acidified sample is filtered. The filter is rolled and transferred into an extraction thimble and dried in a hot-air oven at 103⁰C for 30 minutes. An extraction flask is weighed and 100mL of n-hexane solvent is added. Oil and grease is extracted in a Soxhlet apparatus at a rate of 20cycles/hour for 4 hours.
3. Extraction Method for Sludge Samples (5520 E): Sludge samples are acidified with 1mL concentrated HCl/80g sample to bring the pH to 2 or less. 20±0.5g of sludge sample, for which the dry solids content is known, is taken in a 150mL beaker. 25g of magnesium sulfate monohydrate is added to the sludge and stirred to a smooth paste and spread on the sides of the beaker to allow it to solidify. Solids are removed and ground in a mortar and transferred into a thimble. Extraction flask is tared and 100mL n-hexane solvent is added. Sample is extracted in a Soxhlet apparatus at a rate of 20cycles/hour for 4 hours. The extracted sample is analyzed by Standard Method 5520 F.
4. Solid-phase, partition-gravimetric method (5520 G): This method is an alternative to liquid-liquid extraction technique or for samples which tend to form emulsions with solvent. Oil and grease are extracted from water samples by passing through solid-phase extraction (SPE) disk or cartridge. The oil and grease are adsorbed by the disk and finally eluted with n-hexane. This method is not applicable to hydrocarbons that

volatilizes at temperature below 85⁰C and also for the petroleum constituents which are not soluble in hexane solvent.

One of the above extraction steps are used for the extraction and determination of oil and grease. But, when petroleum hydrocarbons are of interest, extracted oil and grease is dissolved in 100mL n-hexane. An appropriate amount of silica gel (3.0g of silica gel/100mg oil and grease) is added and stirred for 5 minutes using a magnetic stirrer. The solution is filtered through filter paper and the solvent is vaporized in a tared dish for gravimetric measurement of petroleum hydrocarbon.

2.2.3.2 Partition-Infrared Method (Standard Method 5520 C)

This method makes use of trichlorotrifluoroethane as the extraction solvent which allows the absorbance of the carbon-hydrogen bond in the infrared region of the electromagnetic radiation for the determination of the petroleum hydrocarbon. The sample acidified to pH less than 2 is extracted with trichlorotrifluoroethane solvent thrice and is extracted into a flask by filtering through 10 g sodium sulfate to remove any moisture content. The final volume of the extracted sample is made up to 100mL using the solvent. When petroleum hydrocarbons are to be measured, the extract is stirred with an appropriate amount of silica gel to remove the fatty matter which is not of petroleum origin. The absorbance of samples is measured from 3200cm⁻¹ to 2700 cm⁻¹ and comparing it with the absorbance of known oil standards or reference oil standards (if oil identity of the samples is unknown).

Elimination of evaporation step makes it useful for the analysis of the volatile constituents of petroleum. A mixture of No.2 fuel oil and Wesson oil has showed a

recovery of 99% with a standard deviation of 1.4 mg (Standard Methods for the examination of water and wastewater, 21st Edition).

Two methods for the analysis of total petroleum hydrocarbon have been used for the comparison study. The section below describes the principle behind the methods.

2.2.3.3 EPA Method 1664 Revision A: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravity

This method is based on the prior EPA method for the determination of “oil and grease” and “total petroleum hydrocarbon”. The method is used for the determination of n-hexane extractable material (oil and grease) and n-hexane extractable materials which are not adsorbed by silica gel in surface and saline waters and industrial and domestic aqueous wastes. The definitions of both HEM and SGT-HEM depend on the procedure used. The determination of these method defined analytes can be influenced by the nature of oil and grease, and the presence of extractable oily matter in the sample. Extractable materials include non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related materials.

Method 1664A employs liquid-liquid extraction (LLE) with a separatory funnel as the means for extracting oil and grease from the water. The extracted samples were subjected to Kuderna-Danish concentration which is followed by silica gel treatment for the removal of polar compounds. The silica gel treated sample is dried in a dish and the remaining extract is desiccated and weight of SGT-HEM is determined.

2.2.3.4 Ultraviolet Fluorescence Spectroscopy and the SiteLAB UVF-3100A

The UVF-3100A is a field measurement device capable of determining total petroleum products in water and soil. Measurement of total petroleum hydrocarbon by this

technique generally involves the extraction of TPH using an appropriate solvent followed by the measurement of TPH in the extract using the optical method. Optical measurement made using the UVF-3100A is based upon ultraviolet fluorescence spectroscopy. Aromatic hydrocarbons will fluoresce when they are excited by ultraviolet light and the fluorometer can measure the concentration in the sample extracts.

Electronic Excitation and Attendant Fluorescence

Fluorescence radiation can be defined as the radiation emitted in a transition between the two lowest singlet states. Aromatic compounds in the solvent can be excited directly by monochromatic UV radiation. When a molecule absorbs electromagnetic radiation, its energy increases by an amount equal to the energy of the absorbed photon. This adsorption and emission processes is shown by the Jablonski diagram shown as Figure 2.2.

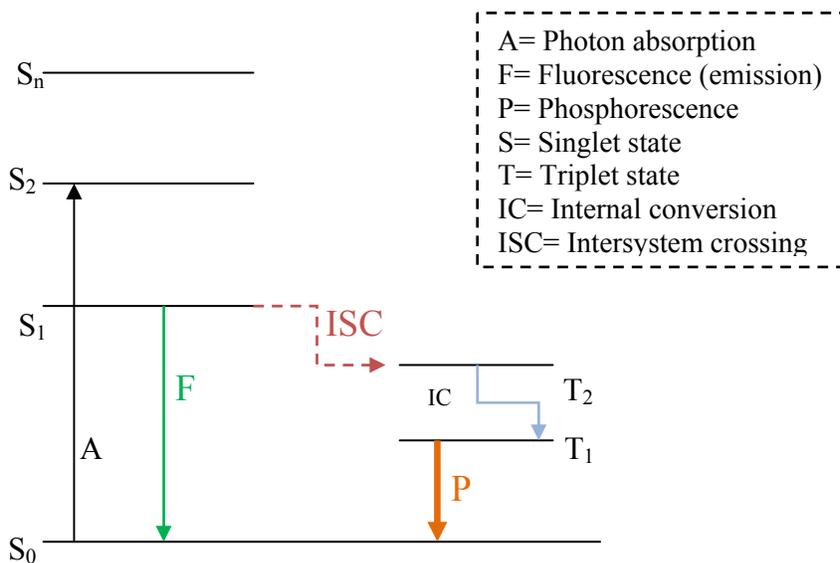


Figure 2.2 Jablonski diagram

Since Ultraviolet Fluorescence Method is concerned with aromatic hydrocarbons, focus is on π -electron transitions. The S's represents the singlet states with net spin angular

momentum zero and T's represent triplet levels with one unit of spin angular momentum. Each electronic level is made up of many vibrational and rotational levels. When a photon with enough energy to cause the excitation in molecule, an electron is raised from the zero vibrational level of the ground state to one of the several vibrational levels of the first excited state ($S_0 \rightarrow S_1$ or $S_0 \rightarrow S_2$). In a liquid medium, an electron in a high vibrational level (e.g. S_2) rapidly loses its excess vibrational energy in collision with neighboring molecules, a process called *vibrational relaxation*. If the molecule can remain in lowest excited state, S_1 for 10^{-9} seconds or longer and there is no competing processes, then the situation is good for the molecule to emit fluorescence radiation. The transition leading to the *fluorescence* takes place from the zero vibrational level of the first excited state to one of the vibrational levels of the ground state.

Beer's Law

Beer's law governs the relationship between the concentration of the fluorescent sample extract and the amount of ultraviolet radiation absorbed by the absorbing species at specific wavelength. Beer's law states that as concentration of the absorbing species increases, the absorbance increases. If c is the concentration of the absorbing species in terms of molarity, the Beer's law can be given as

$$\text{Absorbance, } A = \epsilon lc$$

where ϵ is the molar absorptivity and l is the path length of light

So, according to Beer's law the absorbance of the aromatic hydrocarbons in the sample extract is directly proportional to the concentration of the absorbing aromatic hydrocarbon species and the path length of the ultraviolet light that is transmitted through the sample extract.

3 Materials and Methods

This section describes the preparation of artificial samples, collection of surface water samples, analytical methods and the quality control procedure.

3.1 Supplies, Reagents & Solutions

Sample collection bottles: Brown HDPE, approximately 1L bottles were used for sample collection. The bottles and screw caps were washed with detergent and tap water followed by rinse with dilute H₂SO₄ solution, 3 times with distilled water and 3 times with deionised water respectively. Since the bottles could not be baked in an oven, they were rinsed with n-hexane to remove any residues that might interfere with the analysis.

Reagent water: Deionized water in which hexane extractable material is not detected.

Sulphuric acid solution: 1 part concentrated H₂SO₄ and 3 parts reagent water was mixed together to produce approximately 6N solution which was used for adjusting the pH.

Solvent: acetone, n-hexane, methanol and cyclohexane of HPLC grade were used as solvents

o-terphenyl: 98% pure chemical was purchased from Alfa Aesar

p-terphenyl: 99%+ pure chemical was purchased from Alfa Aesar

Stearic acid: 99% pure compound was obtained from Alfa Aesar

Silica gel: Anhydrous silica gel of chromatographic grade of 80-200 mesh was used for removing the polar constituents from the extract. It was dried in 105⁰C oven and desiccated and stored in sealed container.

Motor Oil: Formula Shell SAE10W-30 Motor Oil for gasoline engines.

No.6 Fuel Oil: Fuel oil was purchased from Subsurface Environmental Solutions LLC, Andover, MA.

3.2 Sample collection, Preservation and Storage:

Surface water samples were used in this study. Ortho-terphenyl and stearic acid, o-terphenyl, p-terphenyl, lubricating motor oil and No.6 fuel oil were used to prepare the artificial samples. Surface water samples of approximately 1L collected from the surface in wide-mouth brown HDPE bottles as grab samples. On reaching the laboratory the samples were adjusted to pH less than 2 using 1mL of 6N sulfuric acid solution and were refrigerated at temperature less than 4⁰C until extraction. The samples were analyzed before the holding time of 28 days.

3.3 Preparation of Artificial Samples

Artificial samples used in this study were prepared from o-terphenyl and stearic acid, o-terphenyl, p-terphenyl, lubricating motor oil and No.6 fuel oil. 1,2-diphenylbenzene (C₁₈H₁₄) commonly known as o-terphenyl, and stearic acid were used to prepare the artificial samples for the quality control studies. All other chemicals and oils were only used for preparing artificial samples for comparing the analytical methods. The physical properties of the compound are summarized in the Table 3.1.

Table 3.1 Physical Properties of chemicals used

Properties	o-terphenyl	p-terphenyl
Boiling point	332 ⁰ C	376 ⁰ C
Melting point	56 ⁰ C	213 ⁰ C
Flash point	163 ⁰ C	207 ⁰ C
Specific density	1.1	1.23
Vapor pressure, P _a at 25 ⁰ C	0.0033	-
Solubility in water	Insoluble	Insoluble

Although the EPA Method 1664 suggests using hexadecane, o-terphenyl was used in preparing the spiking solution as the UVF method responds only to aromatic hydrocarbons. o-terphenyl/ stearic acid (1:1) spiking solution of concentration 2g/L was prepared by weighing 200 ± 2 mg stearic acid and 200 ± 2 mg o-terphenyl in a 100mL volumetric flask and making up to the mark with acetone. The solution was stored in a dark at room temperature. The spiking solution was checked for evaporation and was brought to volume prior to use.

3.4 Analytical Methods

In this study, two methods were used for the analysis of artificial samples as well as petroleum hydrocarbon contaminated surface water.

3.4.1 EPA Method 1664, Revision A

EPA Method 1664, Revision A, is a liquid/liquid extraction (LLE), gravimetric procedure that employs normal hexane (*n*-hexane) as the extraction solvent, replacing 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) of Method 9070, a Class 1 CFC, for determination of oil and grease and for the determination of non-polar material (NPM) as silica gel treated *n*-hexane extractable material (SGT-HEM). Method 1664, Revision A is an empirical method applicable to aqueous matrices that requires strict adherence to all the details for precise and accurate results. The method is not applicable to measurement of low-boiling fractions that volatilize at temperature below approximately 90°C. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.

The method consists of following steps for the analysis of samples:

1. Bring the analytical batch of samples to room temperature.

pH Verification: Verify the pH of the sample is less than 2 by following procedure:

2. Dip a glass stirring rod into the well mixed sample
3. Withdraw the stirring rod and allow a drop of the sample to fall on the pH paper.
If necessary add more H_2SO_4 solution to the sample. Replace the cap and shake the bottle to mix thoroughly and retest for pH verification.

Extraction:

4. Pour the 1-L sample into a separatory funnel.
5. Add a 60mL of n-hexane to the sample bottle and seal the bottle with original bottle cap. Shake the bottle to rinse all the interior surfaces of the bottle including the lid. Pour the solvent into the separatory funnel.
6. Extract the sample by shaking the separatory funnel vigorously for 2 minutes with periodic venting into the hood to release excess pressure.
7. Allow the organic phase to separate from the aqueous phase for a minimum of 10 minutes.
8. Drain the aqueous layer (lower layer) into an Erlenmeyer flask. Drain a small amount of the organic layer into the flask to minimize the amount of water remaining in the separatory funnel. The amount of water remaining with the n-hexane must be minimized to prevent dissolution or clumping of sodium sulfate in the filtration step.
9. 4-6 boiling chips are added to the concentration vial attached to Kuderna-Danish. Place glass wool into the bottom of funnel and add about 20g of sodium sulfate.

Wet the sodium sulfate with 20ml of hexane. Drain the n-hexane layer through the sodium sulfate and collect into the concentration vial. Repeat the extraction twice more using fresh portions of 60mL hexane each time.

Solvent Concentration:

10. Snyder Column is connected to the head of Kuderna-Danish. The concentration vial and lower half of the Kuderna-Danish is immersed in a water bath and the temperature is kept around 90⁰C. When the contents in the vial reach almost 8mL it is removed from the water bath.
11. Prepare a Pasteur pipette micro-column plugged with glass wool and filled with approximately 1/3rd height of the long stem with silica gel and rest with little sodium sulfate. Pre-elute the silica gel with hexane and discard. Pass the concentrated sample through the silica gel and collect in a pre-weighed aluminum dish. Rinse the concentration vial a few times with hexane and add to the silica gel collecting all the solvent into smooth walled aluminum dish.
12. Place the aluminum dish in a fume hood to evaporate the hexane. The aluminum dishes are removed from the hood as soon as they start to develop dry spots and is placed in a desiccator to continue drying for 30 minutes. Reweigh the dish to determine the weight of the TPH as soon as the solvent is completely dry.

3.4.1.1 Quality Control

The quality assurance procedure consists of an initial demonstration of laboratory capability, ongoing analyses of standards and blanks as a test of continued performance. Initial demonstration of the laboratory capability consist of a establishing a Method Detection Limit using standards. As part of the ongoing precision and recovery study,

analysis of laboratory spikes and laboratory blanks are done to demonstrate that the analysis system is in control. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

Method Detection Limit (MDL) Study for EPA Method 1664, Revision A:

The expected MDL for the EPA Method 1664 A is 1.4mg/L for SGT-HEM.

Procedure:

1. Prepare laboratory standard at a concentration which is at least equal to the estimated MDL (1.4mg/L) by spiking reagent grade water with o-terphenyl and stearic acid spiking solution.
2. 2 aliquots of the above standard are processed through the entire analytical method (extraction of TPH using hexane, concentration in Kuderna-Danish, silica gel treatment, final weight measurement).
3. If these measurements indicate the sample is in desirable range for determination of MDL, 5 additional aliquots are processed. All these 7 sample measurements are used for the calculation of MDL.
4. If the measurements from the 2nd step indicate that the sample is not in correct range, obtain new sample as in the step 1 and repeat steps 2 and 3.
5. Calculate variance (s^2) and the standard deviation (s) of the replicate measurements.
6. $MDL = t_{[n-1=6, 1-\alpha=0.99]}S = 3.14*s$

3.4.2 UVF-3100A and TPH Analysis

SiteLAB's UVF-3100A is a field measurement device which uses optical measurements based on ultraviolet fluorescence spectroscopy for the determination of petroleum contaminants. The analyzer includes a portable fluorometer fitted with excitation and emission filters that are appropriate for the TPH analysis. The arrangement of the equipment for exciting, detecting and recording the spectrum of the emitted radiation is shown in the Figure 2.3.

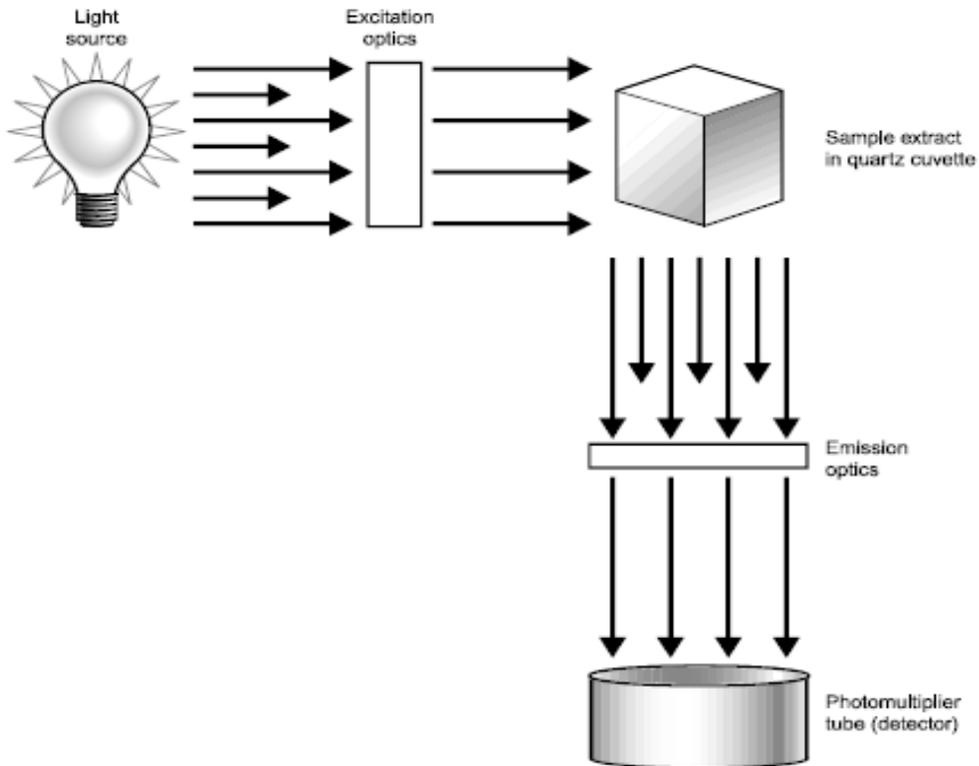


Figure 3.1 Schematic diagram of Ultraviolet Fluorescent Spectrometer (Source: SiteLAB's Innovative Technology Verification Report)

In UVF-3100A, a multiple wavelength mercury lamp that emits light in the ultraviolet range, predominantly at 254nm is used as the light source. The light passes through a monochromator which reduces the broad-wavelength light beam to a single wavelength

(254nm) beam. The single wavelength beam coming out of the monochromator is focused by means of a quartz lens at normal incidence on the surface of the cuvette holding the scintillation solution. Fluorometer has an emission filter in the band width of 300nm to 400nm. The emitted radiation passing through the emission filter is received by the photomultiplier tube which aid as the detector for the instrument. The instrument is calibrated using TPH-Oil calibration standards (CAL-057) made from a certified grade of non-synthetic motor oil and its composition is proprietary. The calibration is based on the fluorescence property of the aromatic compounds present in the calibration standards. Alternatively, if the TPH present in the sample is known, the instrument can be calibrated using the specific fuel oil or the aromatic compound which make the sample extract. The sample extracts are measured for the optical property against the generated calibration curve.

The steps for the analysis of sample using UVF-3100A are explained below:

1. Bring the analytical batch of samples to room temperature.

Extraction:

2. Pour 10mL of sample to a mixer can.
3. Add 10mL of methanol to the mixer can and shake it manually to produce a uniform sample with methanol.

Optical measurement:

4. A syringe with detachable filter was used to transfer the extracted sample to the quartz cuvette.

5. The cuvette was placed in the chamber of the fluorometer. The extract was analyzed and the device displayed the TPH concentration in parts per million. If the sample was diluted using the solvent other than 1:1, the dilution should be taken care for the calculation of the TPH concentration in the sample.

4 Quality Control Study

This section presents the experimental results of the quality control procedure for EPA Method 1664A, analysis of artificial and natural surface water samples using EPA Method 1664A and SiteLAB's Ultraviolet Fluorescence Technology. The quality assurance program of EPA Method 1664A consists of demonstration of laboratory capability by an initial precision and recovery study, determination of method detection limit, analysis of ongoing precision and recovery samples as a test of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of the analyses meet the performance characteristics of the method.

4.1 Initial Precision and Recovery (IPR) Study

4.1.1 IPR Experiment 1

Initial Precision and Accuracy tests are performed to establish the ability to generate acceptable precision and accuracy of the analysis. Precision and recovery (PAR) standards of concentration approximately 20mg/L were made by pipeting 10mL of o-terphenyl/stearic acid spiking solution into approximately 1L of deionised water. Concentrations of silica gel treated hexane extractable material (SGT-HEM) in four samples of PAR standard are analyzed according to the procedure for EPA Method 1664A described in section 11 of the Document No.EPA-821-R-98-002. The procedure consists of mainly three steps: liquid-liquid extraction using separatory funnel, solvent distillation using Kuderna-Danish for the concentration of hexane extractable material and silica gel treatment. The Table 3.1 presents the results obtained.

Table 4.1 Initial Precision and Recovery (IPR) study for EPA 1664A

Sample	Concentration (mg/L)	Recovery (%)
Sample 1	6.37	31.85
Sample 2	3.83	19.5
Sample 3	7.35	36.75
Sample 4	3.76	18.8

The acceptance criteria for the initial precision and recovery of SGT-HEM by Method 1664A is that the recovery (X) for a set of four samples of PAR standard should be in the range of 83-116% and the standard deviation (s) should be less than 28%. For the above set of PAR standard the standard deviation is found to be 9.1%. As, X falls outside the range of recovery, the system performance was unacceptable.

4.1.2 IPR Experiment 2

As the Experiment 1 did not meet the acceptable recovery criteria, another set of similar tests were conducted with following changes in the procedure:

1. Volume of hexane used for the extraction of HEM was increased to 60mL each time, instead of 30mL.
2. Anhydrous sodium sulfate was kept in oven and was cooled in desiccator before it was used for the filtration step.
3. Water bath was kept at temperature around 90⁰C for the Kuderna-Danish concentration procedure.
4. Approximately 180mL of hexane containing the hexane extractable material was concentrated in Kuderna-Danish to a volume of 8-10mL instead of approximately 2mL.

The Table 3.2 presents the result for precision and accuracy study conducted with variation in the procedure.

Table 4.2 Results for the IPR Study: 2

Samples	Concentration (mg/L)	Recovery (%)
Sample 1	9.13	45.65
Sample 2	8.45	42.25
Sample 3	8.98	44.9
Sample 4	8.48	42.4

The standard deviation for the set of analysis was calculated to be 1.7%. The recovery results showed 9% increase compared to the recovery in Experiment 1. However, the results did not fall in the acceptable range of recovery for the analysis and the performance was considered unacceptable.

4.1.3 IPR Experiment 3

In this case, to correct the problem, the analysis was stopped after each step to determine the recovery of HEM and SGT-HEM. The changes adopted in the *Experiment 2* were retained in this experiment. To check for the loss of sample, the procedure was divided into three steps: extraction, concentration and silica gel treatment followed by evaporation. The Table 3.3, 3.4 and 3.5 represents the results obtained from analysis of set of four each samples.

Table 4.3 IPR study showing HEM results after the extraction step

Sample	Concentration (mg/L)	Recovery (%)
Sample 1	38.4	96
Sample 2	39.0	97.5
Sample 3	40.2	100.5
Sample 4	37.8	94.5

Table 4.4 IPR study showing HEM results after the concentration step

Sample	Concentration (mg/L)	Recovery (%)
Sample 5	40.28	100.7
Sample 6	34.93	87.33
Sample 7	39.65	99.13
Sample 8	38.23	95.58

The Table 3.3 and Table 3.4 shows HEM recovery after solvent extraction and the solvent distillation steps respectively. The acceptance criteria for the initial precision and recovery of HEM by Method 1664A is that, the recovery (X) for a set of four samples of PAR standard should be in the range of 83-101% and the standard deviation (s) should be less than 11%. The average recovery of HEM after the extraction and concentration step is 97.1% and 95.7% respectively. And the standard deviation is found to be 2.56% and 5.97% respectively. Comparing the results of percentage recovery and standard deviation, it is observed that the results meet the acceptable criteria, and the system performance is acceptable for the analysis of hexane extractable material.

Table 4.5 IPR study showing the SGT-HEM results

Sample	Concentration (mg/L)	Recovery (%)
Sample 9	8.19	40.95
Sample 10	10.75	53.75
Sample 11	10.75	53.75
Sample 12	8.85	44.25

From the Table 3.5 the average recovery of SGT-HEM is observed to be 48% and the standard deviation for the set of four samples is 6.6%. The standard deviation met the precision limit but, the percentage recovery fell outside the range of recovery and it was

clear that the SGT-HEM were being lost at the silica gel treatment step or the evaporation step which follows it.

4.1.4 IPR Experiment 4

Another set of four samples were analyzed for SGT-HEM with silica gel half way through the 9-inch Pasteur pipette for the removal of the polar stearic acid from the hexane extractable material. The Table 3.6 represents the results obtained from the experiment.

Table 4.6 The IPR study showing the results

Samples	Concentration (mg/L)	Recovery (%)
Sample 1	10.51	52.55
Sample 2	13.1	65.5
Sample 3	12.4	62.0
Sample 4	12.3	61.5

The experiment showed better results with an average percentage recovery of 60.4% and a standard deviation of 5.5%. The results showed that the performance tests did not meet the acceptance criteria.

4.1.5 IPR Experiment 5

To check for the sample recovery loss, two similar set of three standards were prepared for a qualitative and quantitative test. Standards prepared were the following:

1. 2 mg/mL of stearic acid in hexane
2. 2 mg/mL of o-terphenyl in hexane
3. 4 mg/mL of o-terphenyl and stearic acid in hexane

4.1.5.1 Qualitative Test

Guaiazulene, a hexane soluble dye was added to one set of three qualitative standards. 10mL of each standard was pipeted into separate aluminum pans and was evaporated in a hood and the results were observed. The Figure 3.1 presents the result of the qualitative test.



Figure 4.1 Observation of the evaporation step of the qualitative test

The evaporation of SGT-HEM extract took 30 minutes. The observation showed blue colored dye along the grooves of the fluted walls of the aluminum pan for the o-terphenyl standard. The stearic acid standard and the standard of stearic acid and o-terphenyl did not show signs of dye along the walls of the aluminum pan. This might be due to the solidification of stearic acid as the hexane evaporated from the pan. However, the fluted walls of the aluminum pans had provided enough grooves or surface area for the o-terphenyl standard to climb up and flow out of the pan during the evaporation step in the hood. The solubility of o-terphenyl in the solvent, volatile nature of the hexane solvent and the air flow in the exhaust air hood along with the grooved walls of the pan which

provided a capillary network has aided in the rise of sample extract along the walls of the aluminum pan.

4.1.5.2 Quantitative test

The analytical results from the quantitative standards will aid to indicate where the actual recovery losses are occurring. 10mL of each quantitative standard was pipeted into separate dry standard flasks and was diluted to 100mL with n-hexane. This standard was passed through sodium sulfate-silica gel column and collected in an aluminum pan and was evaporated in a hood and weighed for results. The results are presented in Table 3.7.

Table 4.7 Results of the quantitative tests

Standards	Concentration (mg/L)	Recovery (%)
20 mg/L stearic acid	0.14	0.7
20 mg/L o-terphenyl	14	70
40 mg/L stearic acid and o-terphenyl	16.1	80.5

Stearic acid, the polar material in the standards should be removed completely after the silica gel clean-up procedure. The silica gel treatment has removed 99% of the polar stearic acid in the 20mg/L stearic acid standard. So, the silica gel clean up for the polar compounds has been found to work well. However, it was observed that the sample recovery for the stearic acid and o-terphenyl standard was 80.5% which is less than lower limit of acceptance for a quality control test. This low recovery of sample was also supported by finding in the qualitative test. So, it was decided to use smooth walled aluminum dish for the evaporation purpose.

A similar qualitative and quantitative test was repeated with smooth walled aluminum dish and the results are shown in Figure 3.2 and Table 3.8 respectively.



Figure 4.2 Observation of the qualitative test using smooth walled aluminum pan

Table 4.8 Results of Quantitative test using smooth walled aluminum pan

Standards	Concentration (mg/L)	Recovery (%)
20 mg/L stearic acid	0.22	1.1
20 mg/L o-terphenyl	18.86	94.3
40 mg/L stearic acid and o-terphenyl	18.9	89.5

The evaporation was completed in approximately 30 minutes in the hood. It was observed that the SGT-HEM extract was confined in the aluminum pan. Although the extract was able to rise up from the bottom surface of the pan, it was unable to flow out due to the absence of uneven walls. This observation is supported by the results in Table 3.8 which shows a SGT-HEM recovery in the acceptable criterion range of 83-116%. So, the evaporation step for the analysis was optimized by using smooth walled aluminum pan and also to remove the pan from the hood to a desiccator as soon as dry spots start to develop and continue drying for at least 30 minutes to give the best results.

4.1.6 IPR Experiment 6

An initial precision and recovery experiment was performed with a set of four PAR standards by retaining all the procedural changes which assisted in the better recovery of the non-polar compounds and is described under Section 4.1.5.2. The results are summarized in the Table 3.9.

Table 4.9 Results of final IPR Study

Samples	Concentration (mg/L)	Recovery (%)
Sample 1	20.03	100.15
Sample 2	17.52	87.6
Sample 3	18.43	92.15
Sample 4	18.69	92.45

The results show percentage recovery (X) in between 87-101% for four aliquots and a standard deviation (s) of 5.19%. Since, the SGT-HEM recovery results of the IPR study was found to fall within the range of recovery and the standard deviation for the four samples did not exceed the prescribed limit of acceptance, the system performance was accepted.

4.2 Determination of Method Detection Limit (MDL)

A Method Detection Limit (MDL) study was conducted to establish the lowest concentration at which the analyte can be detected with 99% confidence. An MDL less than or equal to the proposed MDL of the method should be achieved before the analysis of samples can begin. The estimated MDL for the EPA Method 1664A is 1.4 mg/L. The MDL was determined according to the procedure in 40 CFR Part136, Appendix B, which is summarized in Section 3.4.1.1. To determine the MDL, 7 samples of concentration near the expected limit of detection were processed through all the steps of the analytical

method. The concentration of samples for the MDL study is recommended to be in between 1 and 5 times the estimated method detection limit (1.4-7.0 mg/L). Since the MDL was determined in reagent (blank) water, the samples were prepared by spiking deionised water with o-terphenyl/ stearic acid spiking solution, so as to obtain 1L of 5mg SGT-HEM. The results of the study are presented in the Table 3.10.

Table 4.10 Results obtained for the MDL Study

Samples	Concentration (mg/L)	Recovery (%)
Sample 1	5.04	100.8
Sample 2	5.44	108.8
Sample 3	5.69	113.8
Sample 4	4.97	99.4
Sample 5	5.99	119.8
Sample 6	5.66	113.2
Sample 7	5.23	104.6

The mean spike recovery for the o-terphenyl/ stearic acid laboratory standard and the standard deviation (*s*) of the mean concentration measured for the 7 aliquots were found to be 5.43 mg/L and 0.37 mg/L respectively. The MDL is calculated by multiplying the one-sided t distribution with the standard deviation of the replicate analyses, which is basically represented as

$$MDL = t_{[n-1=6, 1-\alpha=0.99]} * s$$

For seven samples (for a standard deviation estimate with six degrees of freedom) the t value for a 99% confidence interval is 3.143. So, the MDL can be computed as follows:

$$MDL = 3.143 * s = 3.143 * 0.37 = 1.17 \text{ mg/L}$$

4.3 Reporting

The method detection limit was determined to be 1.17 mg/L in reagent water matrix and the minimum level of quantitation based on studies conducted at EPA (61 FR 1730) for the method is 5.0mg/L. Results below the MDL is reported as <1.17 mg/L. The results for the SGT-HEM found between the MDL and the quantitation limit are reported with two significant figures, as none of the surface water sample has a concentration greater than 5.0mg/L.

4.4 Ongoing Precision and Recovery Study (OPR)

On an ongoing basis, a 20 mg/L o-terphenyl PAR standard was prepared and analyzed with each analytical batch to demonstrate that the analysis system was in control, and acceptable precision and accuracy was maintained with each analytical batch. The acceptance criterion for the percentage recovery of SGT-HEM is 64-132%. The recovery result obtained should fall within the range of acceptance for the extraction, distillation, silica gel treatment and evaporation processes to be in control. Laboratory blanks were analyzed with each analytical batch to demonstrate freedom from contamination. The OPR samples and laboratory blanks were subjected to the same procedural steps for a regular sample. The results of OPR samples prepared from o-terphenyl and laboratory blanks for this study was found to be within the acceptable range of performance criteria. This indicated that the continued laboratory analyses were within the method precision and accuracy.

4.5 Quality Assurance for UVF Method

The analyses of petroleum hydrocarbons by UVF Method were performed at FSL Associates, Brighton. The lab had performed a Method Detection Limit (MDL) study and

has established a MDL of 0.5mg/L for the TPH aqueous samples. According to Method Detection Limit study, reading below the zero and 0.5mg/l are considered too low to be reported. But, for this research study, all the sample results were reported including the one below method detection limit.

5 Results

This section presents the experimental results of the analysis of natural water and artificial samples using EPA Method 1664A and SiteLAB's Ultraviolet Fluorescence Technology to evaluate the agreement between two analytical methods.

5.1 Experimental results for Surface Water samples:

The surface water samples for the study were collected from the north end of the Island End river located in Chelsea and also from several locations on Charles River. 8 samples were collected for the study purpose. The samples were tested with EPA Method 1664A and UVF Technology. The samples tested with UVF Technology were extracted with hexane and methanol and tested against calibration standards provided by the SiteLAB (CAL-057) in the range 0-10mg/L. The results show that only 3 samples are in the reportable range of EPA Method 1664A. Most of the sample analysis using UVF Method gave a higher results comparing with the EPA Reference Method. A scatter-plot of the results of UVF method against the corresponding results of the EPA reference method is shown in the Figure 5.1. The disagreement between methods is measured by the departure of the points from the bisecting line of the plot. The Figure also shows the detection limits of the two methods. It is observed that the 2 of the 3 samples within the reportable range for both the methods show a maximum of 12% relative deviation from the EPA Method 1664A. One of the samples within the reportable range has shown 132% relative deviation on analysis with UVF Technology when extracted with hexane and 40% relative deviation when extraction with methanol.

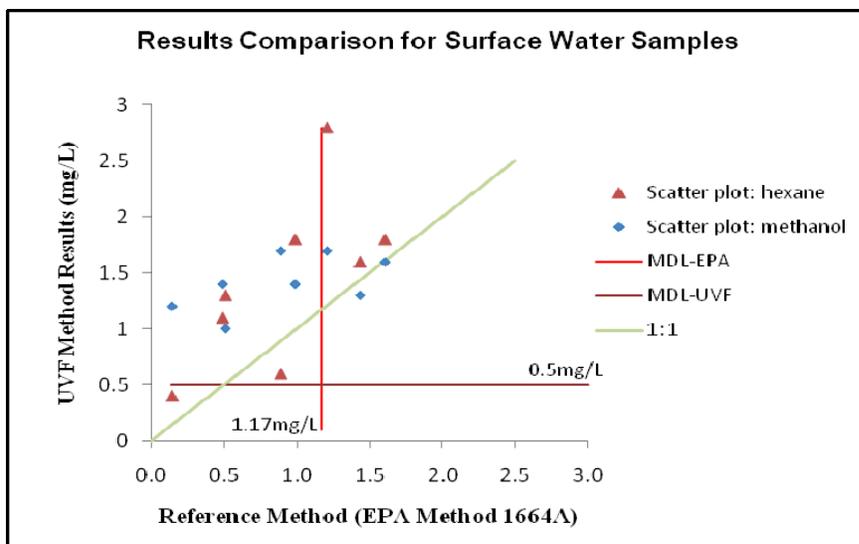


Figure 5.1 Results comparison for the surface water samples

5.2 Experimental results of o-terphenyl and stearic acid samples:

Standards of o-terphenyl and stearic acid were prepared in the range of 1-100mg/L in hexane solvent. The results of the EPA method following the liquid-liquid extraction, concentration and silica-gel clean up give a percentage recovery of 96-105% which is within the acceptable criteria of 64-132% for ongoing precision and recovery. The analysis of samples using ultraviolet fluorescence technology provided results which did not match with the expected values of the working standards. Analysis of samples in the range of 1-100mg/L o-terphenyl and stearic acid gave results in the range from 1.4 -0.0 mg/L. It was observed that the analysis of the samples showed a decrease in fluorescence property with increase in concentration. The plot of results for the EPA Method and UVF method against the expected value of the working standard solutions are given in the Figure 5.2

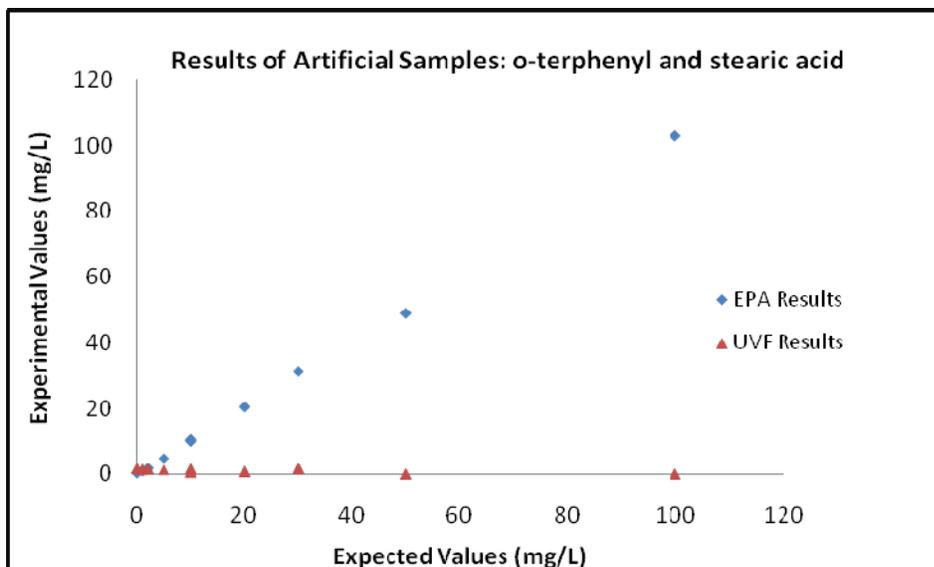


Figure 5.2 Results comparison for the o-terphenyl and stearic acid samples

5.3 Experimental results of o-terphenyl samples:

Another set of analysis was conducted with o-terphenyl standards without stearic acid to check for any fluorescence quenching effect due to stearic acid. The analysis was conducted with 9 o-terphenyl working standards in the range 1-100mg/L. The samples were prepared in hexane and methanol solvents. The results of the analysis are shown in Table 5.1.

Table 5.1 Results for the analysis of o-terphenyl using UVF Method

No:	Sample ID	Expected Concentration (mg/L)	Solvent	
			Methanol (mg/L)	Hexane (mg/L)
1	Sample 1	1.0	0.0	0.8
2	Sample 2	2.0	0.0	0.8
3	Sample 3	5.0	0.0	0.6
4	Sample 4	10.0	0.0	0.4
5	Sample 5	10.0	0.0	0.4
6	Sample 6	20.0	0.0	0.1
7	Sample 7	30.0	0.0	0.1
8	Sample 8	50.0	0.0	0.0
9	Sample 9	100.0	0.0	0.0

The o-terphenyl samples in methanol has shown no response of fluorescence property at 254nm. The o-terphenyl samples prepared in hexane showed fluorescence property, but at a lower rate than the samples containing stearic acid and it showed similar property of decrease in fluorescence with increase in concentration. This explained that stearic acid has no effect on quenching the fluorescence in the previous set of experiments with o-terphenyl and stearic acid solutions.

The decrease in light emission with increase in molecule concentration was studied by H. Kallmann and M. Furst in 1951. The study showed the presence of self or resonance quenching in which intensity of light emission decreases with the concentration of the fluorescent molecules for a constant amount of absorbed light energy. Self-quenching interaction happens due to the resonance between same or similar molecules. This happens when an unexcited molecule approaches and collides with an excited molecule and the energy may be transformed into heat or the two molecule may form an excited double molecule with energy lost in the binding process and also in the interaction with the surroundings. The double molecule has lower probability for light emission than the isolated molecule. With increase in concentration of the fluorescent molecule in the solvent the probability of the states of lower energy increases by the factor exponentially proportional to the energy difference between the two states which increases with increasing concentration. So, the increase in concentration must suppress the probability of light emission. H. Kallmann and M. Furst have observed radiation quenching at a concentration at 100mg/L of o-terphenyl in xylene. Similar observation has been observed in the experiment done with o-terphenyl in hexane solvent. Consequently, comparison of methods using o-terphenyl standards became unfeasible.

5.4 Experiments using Formula Shell 10W-30 Motor Oil

5 samples of Formula Shell 10W-30 Motor Oil in the concentration range of 1-15mg/l were analysed using EPA Method and UVF Method. The results of the analysis are given in the Table 5.2. On comparison with the expected concentration, the results of the EPA Method show a percentage recovery of 102-113% for the results in the reportable range. A higher percentage recovery of 131% is observed for the concentration below the method detection limit of EPA Method. But, it is found to be within the acceptance criteria for ongoing precision and recovery performance tests of EPA Method 1664A.

Table 5.2 Results for the analysis of Motor oil

No:	Sample ID	EPA Method (mg/L)	Expected Concentration (mg/L)	UVF Method	
				Methanol (mg/L)	Hexane (mg/L)
1	Sample 1	2.27	2.0	0.0	0.9
2	Sample 2	5.42	5.0	0.1	1.0
3	Sample 3	5.03	5.0	0.1	1.0
4	Sample 4	10.26	10.0	0.2	1.1
5	Sample 5	15.38	15.0	0.5	1.2

Samples analysed using UVF Method was prepared in hexane and methanol. The observed results were much lower in comparison with the expected concentration. The analysis of samples in the range of 2.0-15.0mg/L gave results ranging from 0.9-1.2mg/L for samples prepared in hexane and 0.0-0.5mg/L for samples prepared in methanol.

Material Safety Data Sheet of the Formula Shell 10W-30 Motor Oil states that it is a highly refined mineral oil containing hydrotreated light paraffins which contains <3% w/w of DMSO extract. The mineral oil is mainly composed of alkanes, typically C₁₅ to C₄₀ carbon atoms. Alkanes are not detected by SiteLAB's UVF Technology.

5.5 Experiments results of No.6 Fuel Oil:

10 samples of No.6 fuel oil in the range approximately equal to 0.5- 20mg/L were analysed using EPA Method and UVF Technology. The samples were prepared only in hexane as the fuel oil was found to be almost insoluble in methanol. Table 5.3 represents the results of the analysis.

Table 5.3 Results for the analysis of No.6 Fuel oil

Sample ID	Concentration Expected (mg/L)	EPA Method results (mg/L)	UVF results (mg/L)
A	0.503	-	2.6
B	1.006	0.74	5.1
C	2.012	1.73	10.3
D	5.03	4.62	Over the range
E	5.03	4.50	Over the range
F	8.048	7.24	Over the range
G	10.06	9.08	Over the range
H	12.072	10.90	Over the range
I	15.09	13.70	Over the range
J	20.12	17.6	Over the range
K	0	0.22	0

All the results from the EPA Method are below the expected value. The recovery is 73.0-92.0%. The recovery was closer to the lower limits of the acceptance criteria (64-132%) for ongoing precision and recovery samples. This can be due to the presence of polar constituents in the fuel oil. The Material Safety Data Sheet of the No.6 fuel oil states that 3% by weight of fuel oil is polar compounds. This could be removed by the silica gel clean up step of Method 1664A. Of the 10 samples analysed using UVF technology, only 3 samples were found to be within 0-10mg/L of the calibration range. The sample concentrations in the range approximately equal to 0.5-20mg/L using the UVF technology yielded 5 times higher values on comparison with the expected concentration.

According to the Technical Report by the United States Mineral Management Service and Environmental Emergency Division of Canada (Catalogue of Crude Oil and oil product properties (1990 Version)), No.6 fuel oil typically contains 24.4% of saturates, 54.6% of aromatics and 6.17% of asphaltenes of the total weight. Unsaturated organic compounds like aromatics are essentially responsible for the fluorescence of fuel oils. The complex blend of high molecular weight compounds include appreciable amounts of naphthenic hydrocarbons, polynuclear aromatic compounds and asphaltenes. The UVF Technology compares the fluorescence property of the aromatic compounds at 254nm to concentration of aromatics present, it implies that each unit weight of this sample of No.6 fuel contains 5 times more aromatics than the TPH-Oil calibration standards.

5.6 Experimental results of p-terphenyl samples:

Samples of p-terphenyl were analysed using EPA Gravimetric Method and UVF Technology. The results of the EPA Method are shown in Table 5.4. The results of the analysis give a percentage recovery of 94-114% in the reportable range of the EPA Method.

Table 5.4 Results for the analysis of p-terphenyl using EPA Method

Sample ID	Expected Concentration (mg/L)	EPA Method (mg/L)
Sample A	1.0	0.90
Sample B	2.0	2.2
Sample C	5.0	5.1
Sample D	5.0	4.7
Sample E	10.0	11.4
Sample F	12.0	13.7

n-hexane was used as solvents for preparing the samples for UVF Method. 1mg/L of p-terphenyl in hexane analysed by UVF method was over the range of the spectrometer

calibration. So, 7 samples of p-terphenyl in hexane solvent in the concentration range of 0.01-0.09mg/L were analyzed using UVF method. These samples were not analysed using EPA Method as the concentrations were below the Method Detection Limit established. The results of the UVF analysis are given in the Table 5.5. It was observed that all the analytical results were approximately 100 times greater than the expected concentration for the samples.

Table 5.5 Results of the analysis of p-terphenyl in n-hexane using UVF Method

Sample ID	Expected Concentration (mg/L)	UVF (Solvent: hexane) (mg/L)
Sample A	0.01	1.1
Sample B	0.02	2.5
Sample C	0.05	6.4
Sample D	0.05	6.5
Sample E	0.06	7.9
Sample F	0.08	11.05
Sample G	0.09	Over the range

Aromatic hydrocarbon substituted by unsaturated phenyl groups exhibit a larger fluorescence property compared to similar molecules without substituents. p-terphenyl molecule is a system of delocalized 18 π -electrons and shows ultraviolet absorption at its peak at 276nm. Studies on the fluorescence emission property of p-terphenyl molecule has been reported (Berlman, 1965). The Figure 5.3 represents the absorption and fluorescence curves of p-terphenyl in cyclohexane solvent at 303nm.

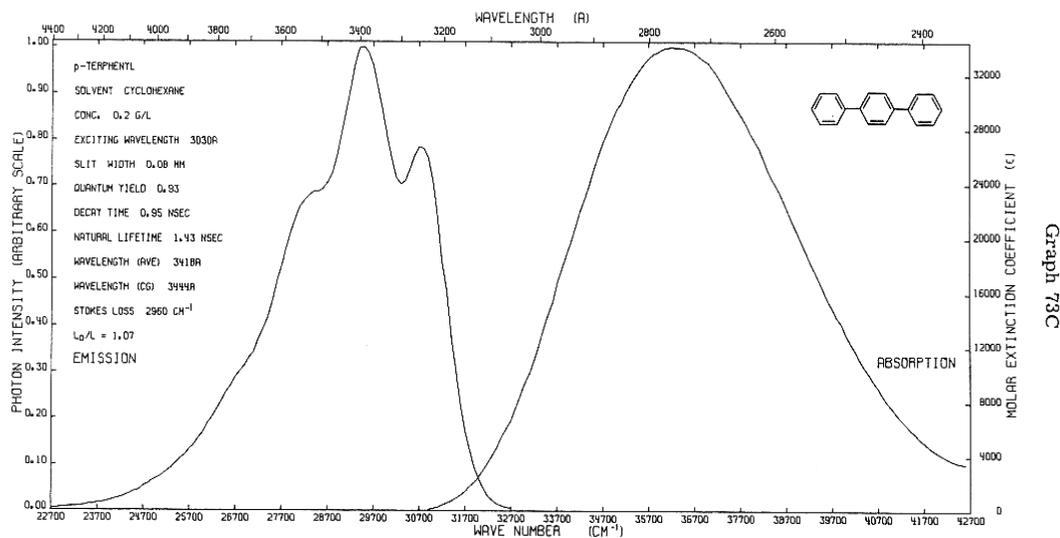


Figure 5.3 Absorption and fluorescence curves of p-terphenyl (Source: Handbook of fluorescence spectra of aromatic molecules, Berlman, I.B, 1965)

The results of the study showed that p-terphenyl has a uncorrected relative fluorescence quantum yield of 0.93 comparing with 9,10-diphenyl anthracene. 9,10-diphenyl anthracene is assumed to have a quantum yield of 1.0 as it is one of the few molecules which do not exhibit fluorescence quenching in solvents. So, p-terphenyl is found to produce appreciable fluorescence emission in the UV region of electromagnetic radiation. p-terphenyl samples in cyclohexane was analysed to compare the results of UVF Methods in different solvents. The results of the analysis is shown in the Table 5.6.

Table 5.6 Results of the analysis of p-terphenyl in cyclohexane using UVF Method

Sample ID	Expected Concentration (mg/L)	UVF Method (cyclohexane) (mg/L)
Sample G	0.0	0.0
Sample A	0.01	1.3
Sample B	0.05	6.6
Sample C	0.05	6.6
Sample D	0.075	8.5
Sample E	0.1	12

The results of the analysis show a similar result of a factor of 100 times higher concentration results. Its evident from the analyses of p-terphenyl samples that a unit concentration of p-terphenyl is capable of producing 100 times fluorescence than that of the same concentration of the calibration standard used in the UVF Method. The results would have been comparable if the spectrophotometer was calibrated using standards of p-terphenyl instead of SiteLAB's TPH-Oil calibration standards. Also, there have been studies which suggests p-terphenyl as a reference standard for calibrating instruments which make use of the fluorescence property in the ultraviolet range.

6 Conclusions

The purpose of this study was to compare EPA Method 1664A and Ultraviolet Fluorescence Technology for the analysis of total petroleum hydrocarbons in aqueous samples. Known concentrations of different hydrocarbon samples were analyzed using both analytical methods and the concentration data obtained from the analyses were compared with the expected concentration to estimate the analytical recovery for the particular method.

The research utilized EPA Method and the required Initial Precision and Recovery (IPR) was attained in the study conducted for the EPA Method 1664A. The Method Detection Limit (MDL) is calculated to be 1.14 mg/L for EPA Method 1664A. The analysis of the artificial and surface water samples were found to be in compliance with the ongoing precision and recovery performance criteria.

Surface water samples and those prepared from o-terphenyl, stearic acid, p-terphenyl, Formula Shell 10W-30 Motor oil and No.6 fuel oil were used for the comparison study of EPA Reference Method and Ultraviolet Fluorescence Technology. The surface water samples analyzed using EPA Method and UVF Technology gave comparable results in the reportable range for two samples. One of the samples in the reportable range showed a relative difference of 40% on methanol extraction and 132% on hexane extraction with the EPA Method.

The analysis of o-terphenyl and p-terphenyl using EPA Method showed a recovery of 96-105% and 94-114% respectively. It was observed that the o-terphenyl and p-terphenyl samples differ in their behavior to ultraviolet excitation. Both the isomers fluoresce at 254nm. The fluorescence property of the para isomer is found to be 100 times more than

that of the calibration standard of same concentration. In contrast, the photochemical behavior of a known concentration of o-terphenyl sample is much less in comparison to the calibration standard of same concentration. It is observed that an increase in concentration of o-terphenyl is accompanied by decrease in quantum yield of its fluorescence, a phenomenon called self quenching. This indicates that o-terphenyl might not be good standard for the comparison study due to formation of *excimers* which leads to concentration quenching. The analysis of p-terphenyl is possible using Ultraviolet Fluorescence Method, but it is suggested to use the same compound for the calibration of the instrument.

The analysis of samples prepared with Formula Shell Motor oil using the EPA Method gave a recovery of 102-113% in the reportable range of the Method. The motor oil samples exhibited only a weak emission of fluorescent radiation on excitation by ultraviolet light. The motor oil mainly contains hydrotreated light paraffins. Light paraffins are solely straight or branched chain saturated hydrocarbons without any ring structure. Saturated hydrocarbons or alkanes are found not to respond to ultraviolet radiation due to the lack of π -bonds. So, analysis of motor oil containing mineral oils of paraffinic nature cannot be detected using ultraviolet fluorescence method.

The analysis of samples of No.6 fuel oil by EPA Method showed a percentage recovery within 86-92% for the samples in the reportable range. The fuel oil samples recovery are found to be lesser than all other set of samples analyzed. This is likely due to the presence of polar compounds which could be removed during the silica gel cleanup step of the analysis. The analysis of fuel oil samples showed an increase in fluorescence property with increase in concentration. The samples have shown a 5 times greater fluorescence

than the corresponding calibration standard of same concentration which can be interpreted as the presence of more fluorescent species in per weight of fuel oil compared to calibration standards.

It can be concluded that the surface water samples were found to be in agreement with the EPA Method for most of the samples in the reportable limit. The comparison study of EPA Method and Ultraviolet Fluorescence Method were not in agreement for the analysis of o-terphenyl and motor oil samples. The samples of fuel oil and o-terphenyl are showing a greater intensity of fluorescence comparing with the corresponding SiteLAB's calibration standard of same concentration. In general, for comparable results of EPA Method and Ultraviolet Fluorescence Technology, it is advised to generate calibration curve using the site specific petroleum contaminant or any fluorescent species of interest.

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40 Code of Federal Regulations (CFR) Part 136, Appendix B.

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