Minireview Article

A review of techniques for the determination of total petroleum hydrocarbons in soils.

ABSTRACT.

The Total Petroleum Hydrocarbon (TPH) is the total of different types of hydrocarbons in the crude oil mixture. It includes volatile petroleum hydrocarbons and extractable petroleum hydrocarbons. The TPH determination techniques are primarily grouped into spectroscopic (ultraviolet spectroscopy, raman spectroscopy, fluorescence spectroscopy, infrared spectroscopy) and non- spectroscopic (gravimetric, immunoassay, gas chromatography with mass spectrometric detection (GC/MSD), gas chromatography with flame ionization detection (GC-FID)) techniques. Solvent and the sample characteristics determine the efficiency of the techniques. This paper compares spectroscopic (fourier transform infrared spectroscopy and ultraviolet spectroscopy) and non-spectroscopic (gravimetric and gas chromatography) methods in the determination of TPH in soil. Spectroscopic and non-spectroscopic techniques are efficient, but the paper recommends spectroscopic techniques because the techniques are efficient with small operational time, and are safer in occupational health and safety issues. In addition their results are accurate and reliable.

Keywords: Hydrocarbon, Petroleum, Spectroscopic, Non-spectroscopic

1.0 INTRODUCTION

Crude oil is any mix of hydrocarbons found in liquid phase in natural underground reservoirs. Different components of crude oil after distillation include light oils (gasoline and benzene), medium oils (kerosene and diesel) and heavy oils (lubricating oil, greases, hard wax etc). Hydrocarbons with 6 to 10 carbon atoms ($C_6 – C_{10}$) are the light oils, ($C_{10} – C_{28}$) are the medium oils, (C_{28}- C_{36}) are the heavy oils and (C_5-$C_{12)}$ are the volatile petroleum hydrocarbons (VPH) [1].

The Environmental Protection Agency (EPA) method 418.1 is the widespread method for the determination of TPH in soil samples. Solvents for this method include 1,1,2-Trichlorotrifluoroethane (Freon 113), Carbon tetrachloride, N-Hexane, etc. Its shortcomings include disparity in infrared molar absorptivity, infrared dispersal by mineral elements, and ineffective solvent for extraction [2].

Contemporary procedures are on hand for determining TPH in soil and the procedures normally include solute extraction by solvent, thereafter gas chromatograph analysis is widely used. These contemporary techniques are comparatively expensive; hence the EPA method 418.1 is widely used as a test instrument [3]. The frequently extraction methods for the separation of the semi-volatile compounds from water or aqueous samples include votex extraction, EPA 3510 liquid-liquid extraction, micro-extraction, continuous liquid-liquid extraction [4]. Soxhlet extraction, ultra-sonication, votex/mechanical shaking, supercritical fluid extraction etc are usually used for solid sample extraction [4]. Sample and solvent determine the efficiency of the extraction method.

There are spectroscopic and non-spectroscopic analytical techniques. Spectroscopic techniques include ultraviolet spectrophotometer, Raman spectroscopy, fluorescence spectroscopy, infrared (IR) spectroscopy. Non-spectroscopic techniques include gravimetric, immunoassay, gas chromatography with flame ionization detection (GC/FID), and gas chromatography with mass spectrometric detection (GC/MSD) [5].

1.1 INFRARED SPECTROSCOPY(Spectrophotometer)

Spectroscopy is a type of quantitative and qualitative calibration of reflection, absorption or passing electromagnetic energy [6]. In spectroscopic modes, the emitted electromagnetic energy from a light source is collided with the given phenomenon (sample) out of which some are reflected, some are absorbed and passed through it. Organic or inorganic substance with covalent bonds absorbs diverse frequencies of electromagnetic radiation in the infrared region of the electromagnetic spectrum [7]. A molecule of compound absorbs only selected frequency (energies) of infrared radiation and it is excited to a higher energy state. There are no two molecules of different structure that have the same infrared absorption pattern or spectrum because every bond has a unique frequency of vibration. Absorption spectrum of a substance can be obtained by an infrared spectrometer or spectrophotometer. Types of spectrophotometer are fourier transform infrared (FTIR) spectrometer and dispersive infrared spectrometer. FTIR is an analytical technique used to identify organic, polymeric and in some cases, inorganic materials. It uses infrared light to scan test samples and observe chemical properties by identifying the functional entities in the compound or samples. It makes available the infrared spectrum more swiftly than dispersive spectrometer and it is more sensitive [7].

The two infrared (IR) based methods that can be used to determine total petroleum hydrocarbon are EPA 413.2 (for oil and grease) and EPA 418.1 (for petroleum hydrocarbons). EPA 413.2 method is limited in application unlike EPA 418.1 which is extensively acknowledged as a standard method for the measurement of TPH in contaminated sites [8].

The soil spectral reflectance is used within visible (Vis) and near infrared (NIR) ranges at wavelengths (350-2500 nm). The organic carbon is one of the foremost soil properties that are estimated by satellite images and spectroscopic technologies with high precision because the organic carbon is accumulated in surface layer of soil. This property has various spectral behaviors because of the existing complexity in chemistry of organic matters. The strong absorbent characteristics resulting from organic carbon often occur at the wavelengths about 1730 nm (because of presence of C-H) and 2330 nm (due to existing O-H groups) while the weaker absorbent characteristics are also observed at wavelengths range of 1150 to 2390 nm. The spectral reflectance is a function of soil size; it decreases as size of soil particles reduces, it is ideal for measurement of soil property because it is quick, relatively inexpensive, requires minimal sample preparation, nondestructive, in addition it requires no hazardous chemicals [6].

1.2 **ULTRAVIOLET FLUORESCENCE SPECTROMETRY.**

Ultraviolet fluorescence (UVF) spectrometry is a high-speed and important test technique for TPH measurement. The procedure includes solvent extraction and optical measurement of the hydrocarbon molecules via an ultraviolet fluorescence spectrometer [9]. The technique has capacity to distinguish low-molecular-weight aromatic hydrocarbons from high-molecular-weight compounds. Note that aliphatic alkanes do not respond to ultraviolet radiation because they do not have π-bonds so samples with paraffinic oil cannot be identified by this method. It is not ideal for fingerprint analysis because some non-hydrocarbon compounds and analytes can emit at the same wavelength [10]. The choice of solvent is crucial because the solvent and object whose spectrum is being analyzed should not absorb ultraviolet radiation in the same region. The general knowledge of the object is required for information to be obtained from UV spectrum. In absence of general knowledge of the structure, several generalizations can serve as guide. These generalizations are efficient when combined with infrared and NMR data [5].

1.3. GRAVIMETRIC METHOD.

The two fundamental gravimetric EPA techniques are EPA 413.1 for oil and grease and EPA 1664A for silica gel. The procedure for two methods includes solvent extraction, evaporation, and weighing. The challenges of EPA413.1 are the use of Freon 113 (Ozone-depleting substance) as solvent and its incapability to distinguish polar organic matter from the petroleum hydrocarbon fraction (Matthew, 2009). A method EPA 1664A replaces EPA 413.1 because it uses n-hexane as solvent which is flammable but more environmentally friendly and efficient in measurement of total petroleum hydrocarbon in oil and grease polluted samples [11].

1.4 GAS CHROMATOGRAPHY.

Gas chromatography (GC) is a widespread analytical method for separation and analysis of volatile and semi-volatile compounds in a mixture. The advantage of GC over gravimetric and infrared methods is its capacity to provide detailed information of the compound [8]. The preparation of aqueous semi volatile and solid samples are mostly prepared by liquid-liquid extraction and solvent extraction (by soxhlet instrument) techniques respectively. Alumina is used to take away fatty substances in the extract and the petroleum hydrocarbons are separated into aliphatic and aromatic fractions. Each fraction is introduced into a gas chromatograph with a detector (MS or Non-MS), the detector generates signal when substance passes through it. The detectors include flame-ionization detector (FID), nitrogen-phosphorous detector (NPD), flame photometric (FPD), electron capture (ECD), thermal conductivity (TCD), atomic emission(AED), electrolytic conductivity (ELCD)[8]. The analyte is identified by matching the retention time of an individual compound to that of a standard. The gas chromatography with flame ionization detector (GC-FID) is primarily chosen for the measurement of the aliphatic and aromatic fractions because of its relative sensitivity and selectivity for hydrocarbons [13]. Occasionally, aromatic fraction is analyzed with a photoionization detector (PID) although it is entirely selective for aromatic compound and can overestimate [8].

2.0 COMPARATIVE REVIEW PAPERS OF ANALYTICAL TECHNIQUES.

2.1 Gravimetric technique

Mario et al applied an improved gravimetric method in determining TPH in contaminated soil[14]. For Gravimetric method, soxhlet method is usually used for extraction and n-hexane is the extracting solvent, and the extraction is allowed for 8 hours for maximum recovery in ultrasound bath. Silica gel and celite were added to the extract and it was filtered through cotton packed column, thereafter, evaporation of solvent was done in rotary evaporator and the evaporation of the remnant of solvent was carried out in desiccator with heating system. The deposit was weighed and designated as TPH [14]. For improved gravimetry, vacuum system replaces heating system and ultrasound water bath method replaces soxhlet method. For experiment 10 g of soil and 10g of anhydrous Na_2SO_4 were thoroughly mixed, total of 60ml of n-hexane was the solvent and the filtration process was done with glass fibre, rotary evaporator was used for evaporation of hexane and desiccator under vacuum was used in evaporation of remnant hexane. Thereafter, the residue was measured and tagged TPH [14].

The improved gravimetric method saves time, records high concentration of TPH extraction.

However gravimetric method operation is relatively simple, cost effective and straight forward but with high operational time. Due to its sensitivity it is ideal for samples with high concentration of analytes and it has potential to lose low molecular compound [4]. The improved gravimetic method has higher efficiency but the cost is increased and the operations are comparatively complex because vacuum system is introduced to enhance solvent evaporation operation.

2.2 Fourier transform infrared (FTIR) spectroscopy.

Schwartz et al reviewed FITR spectroscopy as a tool for TPH measurement, and the result was weighed against traditional methods [2]. The contaminated soil was prepared by mixing 98.5g of soil with 1.5g of selected petroleum hydrocarbons (octane fuel, diesel and kerosene). Exposure to air was minimized to prevent loss of petroleum hydrocarbon components. Each sample was divided equally into four parts, three parts were sent to the analytical laboratories and one part to FTIR reflectance spectroscopy for analyses.

The results of FTIR method were almost the same with the commercial laboratories with respect to accuracy and the instrument is a viable field test device for accurate measurement of TPH in soil. The method is quick, environmental friendly, and cost effective but it is not suitable for the analysis of soil contaminated by petrol because of high volatility of petrol [2].

Although FTIR spectroscopy gives reliable result, sometimes it gives false information due to presence of non-petroleum compounds in the sample which may create tough absorbance in the infrared range [9]. FTIR spectrometer does not provide adequate information of hydrocarbon present and solvent (Freon) for the operation is an ozone depleting substance [3]. Overestimation of TPH is possible due to disparity in infrared molar absorptivity of petroleum components and infrared dispersion by mineral particles.

2.3 Gas Chromatography (GC)

Solomon et al reviewed the efficiency of gas chromatographic fingerprinting technique and phytotoxicity bioassay in post remediation assessment of residual hydrocarbons in contaminated soil 15]. The biofertilizers used for the remediation were composted water hyacinth, mexican sunflower and bermuda grass. The solvent used was hexane and the extract (hydrocarbon/hexane mixture) was introduced into gas chromatography (GC) for measurement of TPH. For phytotoxicity experiment, seed germination bioassay of remediated soil was carried out using lettuce plant seed (L. Sativum). There was significant reduction in total petroleum hydrocarbon. Gas chromatographic fingerprints before remediation indicated absence of n-alkanes within n-C_2 to n-C_8 region, this may be attributed to natural attenuation processes. Seed germination index was above 65%, indicating that the remediated soil is non-phytotoxic and could support plant life.

GC methods have capacity to identify degraded oil in environmental samples for pattern recognition, and the profile of unresolved complex mixtures (UCM) in the contaminated samples can be adequately characterized and resolved [16]. Overlap of carbon number ranges could be a challenge because a section of the GRO may be reported as DRO and vice versa [8]. Normally it cannot detect compounds below $C_{6,}$ occasional polar hydrocarbons (alcohols, ethers, etc.) and chlorinated solvents may be quantified as TPH [4].

3.0 **CONCLUSION.**

Gravimetric methods, infrared spectrometry (spectrophotometry), ultraviolet spectrometry and gas chromatograph are relatively efficient and environmentally friendly for measurement of TPH. The improved Gravimetric method is efficient but time wasting, the solvent is not ideal for high molecular compounds, and the operation is relatively intricate and costly due to introduction of vacuum system. FTIR was effective, saves time but it has potential to give false result when the cleanup step is not there because some compounds from non-petroleum origin co-extracted may generate strong absorbance in the infrared range. Also no adequate information on the type of hydrocarbon present, besides, the solvent (Freon) used for extraction is a primary source of ozone-layer depleting substance. Chromatographic fingerprinting technique can unravel the identity of the oil and unresolved complex mixtures but the costs of analysis, operational time are comparatively high. Overlap of carbon number ranges is possible because a section of GRO may be reported as DRO and vice versa. The technique does not have the capacity to detect compounds below C_6, and sometimes polar hydrocarbons and chlorinated solvents may be quantified as TPH.

UVF spectrometry is a high-speed and valuable test method for TPH measurement. It has capacity to distinguish low-molecular-weight aromatic hydrocarbons from high-molecular-weight compounds. The choice of solvent is crucial because the solvent and object whose spectrum is being analyzed should not absorb ultraviolet radiation in the same region.

Spectroscopic and non-spectroscopic techniques have some merits and demerits; therefore, there is need for constant review and improvement of the techniques. Although non-spectroscopic techniques are efficient, I recommend spectroscopic techniques because the techniques have better operational time and safer in occupational health and safety issues. In addition their results are accurate and reliable.

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