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<th>Journal:</th>
<th><em>Applied Spectroscopy Reviews</em></th>
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<td>Manuscript ID:</td>
<td>LAPS-2012-0046</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Reviews</td>
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<tr>
<td>Date Submitted by the Author:</td>
<td>22-Sep-2012</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Okparanma, Reuben; Cranfield University, Environmental Science and Technology Mouazen, Abdul; Cranfield University, Environmental Science and Technology</td>
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<tr>
<td>Keywords:</td>
<td>environmental, GC-MS, infra-red spectroscopy, raman spectroscopy, spectroscopy, mass spectrometry</td>
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Determination of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) in soils: a review of spectroscopic and non-spectroscopic techniques

Reuben Nwomandah Okparanma a

a Department of Environmental Science and Technology, Cranfield University, Cranfield, MK43 0AL Bedfordshire, United Kingdom.

Phone: +44 (0) 1234 750111 (ext 2793)

E-mail: r.okparanma@cranfield.ac.uk

Reuben Nwomandah Okparanma is a PhD student in the Department of Environmental Science and Technology, School of Applied Sciences, Cranfield University.

Abdul Mounem Mouazen a, *

a Department of Environmental Science and Technology, Cranfield University, Cranfield, MK43 0AL Bedfordshire, United Kingdom.

Phone: +44 (0) 1234 750111 (ext 2701)

Fax +44 (0) 1234 752 971

E-mail: a.mouazen@cranfield.ac.uk

*Corresponding Author

Abdul Mounem Mouazen, PhD, is a Senior Lecturer and group leader of Agricultural Systems Engineering in the National Soil Resources Institute, Department of Environmental Science and Technology, Cranfield University. Dr. A. M. Mouazen holds a patent right of a tractor-drawn visible and near-infrared (vis-NIR) soil sensor for online proximal soil sensing.
Abstract

In the analysis of petroleum hydrocarbon-contaminated soils for total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH), the role spectroscopic and non-spectroscopic techniques play are inseparable. Therefore, spectroscopic techniques cannot be discussed in isolation. In this report, spectroscopic techniques including Raman, fluorescence, infrared, visible-near-infrared spectroscopies, as well as mass spectroscopy (coupled to a gas chromatograph), and non-spectroscopic techniques such as gravimetric, immunoassay and gas chromatography with flame ionization detection are reviewed. To bridge the perceived gap in coverage of the quantitative applications of the vis-NIR spectroscopy in the rapid determination of TPHs and PAHs in soils, a detailed review of studies from the period 1999 – 2012 are presented. This report also highlights the strength and limitations of these techniques and evaluates their performance from the perspectives of their attributes of general applicability, namely: economic, portability, operational time, accuracy, and occupational health and safety considerations. Overall, the fluorescence spectroscopic technique had the best performance (85% total score) in comparison to others, while the gravimetric technique performed the least (60% total score). Method-specific solutions geared towards performance improvement have also been suggested.

Key words: Petroleum-Hydrocarbons; Soil; Raman spectroscopy; IR spectroscopy; Fluorescence spectroscopy; Mass spectroscopy; Vis-NIR spectroscopy

Abbreviations:

COPC, constituents of potential concern; DRS, diffuse reflectance spectroscopy; EPA, Environmental Protection Agency; FID, flame ionisation detection; GC, gas chromatography; IMA, immunoassay; IR, infrared; MLR, multiple linear regression; MSD, mass selective detector; MVA, multivariate analysis; PAH, polycyclic aromatic hydrocarbon; PLSR, partial

URL: http://mc.manuscriptcentral.com/spectroscopy  Email: jsneddon@mcneese.edu
least-squares regression; RMSECV, root-mean-square error of cross-validation; RMSEP, root-mean-square error of prediction; RMTs, rapid measurement techniques; RPD, residual prediction deviation; SEP, standard error of prediction; TPH, total petroleum hydrocarbon; Vis–NIR, visible–near-infrared

1. Introduction

In both the upstream and downstream sectors of the oil and gas industry, available records show that spillage of crude-oil and its daughter products occurs frequently due to natural and anthropogenic causes (1, 2). Crude-oil spill on land introduces petroleum-based hydrocarbons (PHCs), which negatively impact on soil biological, chemical and physical characteristics. Results of various environmental studies carried out in oil spill areas show staggering levels of environmental pollution and adverse effects on biota due to the hazardous nature of PHCs (e.g. 3–10). Prior to the remediation of the impacted media, a full assessment of the impact of the PHCs on the environment and/or humans is essential to identifying both the chemistry and the areal extent to which the PHCs exceed local threshold limit values (TLV), and providing decision support on the appropriate remedial strategy to adopt for effective clean-up of the environmental media. The hierarchical approach to risk assessment (11–20) reflects the different types of data handling required at each stage in the data gathering process. Whereas tier 1 risk assessment involves, but not limited to, the quantitation of the total petroleum hydrocarbons (TPH) and n-alkanes to establish their risk-based screening levels (RBSLs), tier 2 (i.e. generic quantitative risk assessment) involves the analysis of the proximal composition and distribution of individual polycyclic aromatic hydrocarbon (PAH) fractions and the indicator PAH compounds. Tier 3 involves a more detailed investigation to determine the compound-specific biomarkers in the environmental sample (21).
Over the years, several spectroscopic and non-spectroscopic techniques have been developed for the analysis of TPH and PAH in soil samples but, the most frequently used are immunoassay (IMA), general gravimetry, laboratory-based gas chromatography (GC) with flame ionisation detection (FID) or mass spectrometry (MS), infrared (IR) spectroscopy, Raman spectroscopy and fluorescence spectroscopy. In recent times, though, a couple of equally important innovative methods that has shown significantly reasonable potentials for the measurement of TPH and PAH in oil-contaminated soils is emerging. These include field portable GC/MS (22), and new generation near-infrared analysis (NIRA) with visible and near-infrared (vis-NIR) spectroscopy (23–28). Although it was not until the recent past that some IMA techniques (29, 30), field portable GC/MS systems (22), and vis-NIR spectroscopy (28) were used to detect PAHs in soil samples. Before now, the laboratory-based GC/MS systems, fluorescence spectroscopy and Raman spectroscopy have been used for the analysis of PAH in environmental samples but, the GC/MS systems are mostly preferred because of their relative selectivity and sensitivity (18, 31–33).

It has been widely acknowledged that making informed decisions on remediation requirements after an oil spill incident requires information about hydrocarbon fractions. It also requires that the degree of accuracy achieved by different analytical techniques currently available meet given standards. This of course has to associate with sampling resolution and cost of analysis, as these are crucial factors for a successful evaluation of hydrocarbon contamination in soils. This may explain the spate of recent efforts to evolve innovative analytical techniques that are believed to be economical, rapid, less prone to occupational hazards and capable of high sampling resolution for improved contaminant mapping and refined soil remediation recommendation; even though they still complement the standard analytical techniques. Unfortunately, to our knowledge, there is no review at the moment on environmental diagnostic tools for TPH and PAHs in contaminated soils, which includes
latest advancements on vis-NIR spectroscopic method. Thus, there is a gap in coverage of
well over a decade since the vis-NIR spectroscopic method was first used to measure TPH in
diesel-contaminated field-collected soil samples by Malley et al. (25). We acknowledge, no
less, opinions already expressed by analysts that this might be due to a series of unanswered
questions about the vis-NIR spectroscopic method concerning, for instance, the requirements
in terms of accuracy indicators (e.g. residual prediction deviation (RPD) and root mean
square error of prediction (RMSEP) values) from the industry and/or regulatory agencies for
a method to be applied in routine applications. However, it is believed that it may be a
worthwhile effort having recently published significant improvements regarding the TPH
measurement accuracies of vis-NIR spectroscopic method as well as its ability to measure
relative concentrations of PAH in soils all documented alongside other methods. Of course,
the importance of such information to the industry and/or regulatory agencies cannot be
overemphasised. It is also believed that with more research, a vis-NIR-based operating field
protocol for TPH and PAHs can be developed for routine application.

The objective of this report was to review the traditional spectroscopic and non-
spectroscopic analytical techniques and selected rapid measurement techniques (RMTs)
based on spectroscopy for measurement of TPH and the PAHs in contaminated soils.

2. Analytical techniques for petroleum hydrocarbons in soils

No doubt, analytical methods for petroleum hydrocarbons currently in use are numerous
and would be all too a herculean task to exhaust in one review. This is the reason this review
focused on a selected number of the most frequently used traditional methods and innovative
techniques including the vis-NIR spectroscopic method to drive home the aim of this report.
These methods are distinguishable by the level of analytical details they provide and their
method of application, into: screening techniques, conventional non-specific methods, and
methods for detailed component analysis (36), which may be field- and/or laboratory-based. As earlier stated, there are several field- and laboratory-based analytical methods for petroleum hydrocarbons currently in use but, the most frequently used methods (Table 1) are gas chromatography with flame ionization detection (GC/FID) (EPA Method 8015) or mass spectrometric detection (GC/MSD) (EPA Methods 8270 and 625), infrared (IR) spectroscopy (EPA Method 418.1), petroleum hydrocarbons by immunoassay (IMA) (EPA Methods 4030 and 4035), and gravimetric TPH methods (EPA Method 1664). Others are Raman spectroscopy, fluorescence spectroscopy and vis-NIR spectroscopy.

2.1. Laboratory-based techniques

2.1.1. General gravimetry

Gravimetric methods employ an initial cold solvent extraction step and a final weight-difference step. In-between, though, there may be a further clean-up step with silica gel to remove biogenic material. If it does not involve a clean-up step, it is termed oil and grease (O&G) method but, if it does, it is termed TPH method (31). In the general gravimetric TPH method (EPA Method 1664), soil samples are uniformly graded by sieving, oven-dried at 105 °C for 12 hours, and TPH compounds eluted with n-hexane. The liquid extract (eluate) is contacted with silica gel to remove biogenic polar materials and then evaporated. The residue is retained and weighed, and the weight difference is reported as a percent of the total soil sample on dry weight basis. Because of the presence of suspended solids, EPA Method 1664 recommends using a 0.45-μm filter (31). Being among the earliest methods developed, though obviously one of the fast declining choice methods (37), gravimetric methods have been widely used to determine TPH in contaminated soils (37). Before now, gravimetric methods were described as quick and inexpensive methods but, in a recent study (37), the long time required for complete hexane evaporation, of not less than 60 minutes, “elevates
the energetic costs of the overall procedure”, and analytical losses at higher times that cause negative errors are incurred. The latter limitation corroborates similar findings in earlier studies (36, 38, 39). The extraction efficiency of gravimetric methods, albeit poor, is hugely affected by the type of eluting solvent used (36, 40). Hexane has poor extraction efficiency for higher molecular weight petroleum compounds (31), and low polarity, which causes the co-extraction of natural organic matter containing multiple polar functional groups (37, 41). Consequently, other chlorinated compounds like chloroform (42) as well as toluene (43) have been used as liquid extractant. It is well known that both chloroform and toluene have serious health implications as evident in the risk phrases published in their respective safety data sheets. Additionally, gravimetric methods are non-specific since they give no information about the type of hydrocarbon present (31, 37). As a result, they are not suitable for assessing PAH compounds. Instead, the method is best suited for screening TPH in very oily sludges or samples containing very heavy molecular-weight hydrocarbons since light hydrocarbons (< C_{15}) are easily volatilized at temperatures below 70 to 85 °C during the evaporation step (31). Detection limits for TPH of approximately 50 mg/kg in soils have been reported (31).

2.1.2. Infrared (IR) spectroscopy

This method harnesses the spectra of the stretching and bending vibration associated with a molecule when it absorbs energy in the IR region of the electromagnetic spectrum for property elucidation (31). In the electromagnetic spectrum, spectra of hydrocarbon derivatives originate mainly from combinations or overtones of C-H stretching modes of saturated CH_{2} and terminal –CH_{3} or aromatic C-H functional groups (44). In the IR region, these occur within the wavenumber range of 3000 to 2900 cm^{-1} (~3333 to 3448 nm) or at the specific wavenumber of 2930 cm^{-1} (~3413 nm) (33). Usually, as-received samples are first extracted with an eluting solvent containing no C-H bonds and the eluate is contacted with
silica gel to remove biogenic polar components before being subjected to IR spectrometry. The absorbance of the eluate is then measured at the specified wavenumber and compared against the calibration curve developed for the instrument. The instrument calibration standard usually is a petroleum hydrocarbon of known TPH concentration (31). The primary advantage of the IR-based methods is that they are quick, simple and inexpensive with commonly detection limits of approximately 10mg/kg in soil (31, 45).

Before the advent of gas chromatographic (GC)-based methods, IR-based methods were frequently used to detect TPH in soils (e.g. 46) as it was recognised by the USEPA as an official TPH screening method such as EPA Method 418.1 (36) as well as by the ISO as in ISO/TR 11046 (47). But, following the ban on the use of Freon (also known as 1,1,2-trichlorotrifluoroethane – CFE) as an extracting solvent because of its potentials to deplete the ozone layer, the use of IR-based methods has plummeted over the years (31). Despite the ban, though, a handful of studies can be found in the open literatures on the use of IR-based methods (27, 45, 47). However, its use as a TPH measurement method is no longer supported by international standardisation; ISO for instance, has replaced ISO/TR 11046:1992 by ISO/DIS 16703:2001, which recommends the use of gas chromatography/flame ionization detection (GC/FID) after extraction with a halogen-free solvent (47). ISO/DIS 16703:2001 has been updated since 2004. Apart from the limitations on its use, a major constraint of the IR-based method, according to literatures (36, 48), is the insensitivity of the technique to unsaturated components of weathered hydrocarbons not exhibiting detectable adsorption bands at the monitoring wavelength. Additionally, the use of standard hydrocarbon mixture different from the contaminating oil for prior equipment calibration invariably does not produce true contaminant concentration since different hydrocarbons respond differently to IR spectroscopy, since single hydrocarbon oil may not be suitable as a universal calibration standard (36, 48). This is because the proportion of saturated and unsaturated hydrocarbon
groups varies with each oil derivative and produces correspondingly variable IR
spectroscopic responses (45). The non-specificity of IR-based methods (45) also limits their
suitability for PAH assessments. IR-based methods are prone to interferences; both negative
and positive biases, due to the use of dissimilar calibration standards as the spilt oil, and from
spurious signals due to CH$_3$ groups associated with nonpetroleum sources (31). As stated
previously, multivariate calibration solves the interference problem in general. The accuracy
of IR-based techniques is dependent on the extraction efficiency of the extracting solvent,
which in turn is affected by the type of solvent used (31, 45). Sample porosity also has a
profound influence on IR signal intensity (27).

2.1.3. Gas Chromatography/Flame Ionization Detection (GC/FID)

The origin, principle and techniques of chromatography have been widely documented
(e.g. 49). Succinctly, chromatography is a separation method in which a mixture is applied as
a narrow initial zone to a stationary, porous sorbent and the components are caused to
undergo differential migration by the flow of the mobile phase, a liquid or a gas (49). In gas
chromatography, an inert carrier gas (helium, hydrogen or nitrogen) carries the gaseous
mixture (or if aqueous, liquids with boiling points < 400 °C), which is to be analysed, through
a capillary column onto a detector at the end of the column (31, 49), which allows better
resolution of components in complex mixtures.

In GC/FID method, as-received samples are first refrigerated at 4 °C until extraction, and
dried either chemically (using a suitable drying agent, say anhydrous sodium sulphate) or
physically, in an oven at 105 °C for 24 hours, to remove any residual moisture. TPH
compounds in the dried samples are then extracted employing eluting solvents (e.g. acetone,
dichloromethane, hexane or pentane), and different forms of adsorbents (e.g. silica gel,
alumina or Florisil®) are used for the extract clean-up and fractionation into aliphatics and
aromatics (32) prior to injection into a chromatographic column. Sample extracts are introduced into the capillary column by headspace, purge-and-trap method (for volatile compounds in the range C$_6$ to C$_{25}$ or C$_{36}$) or direct injection method (for the less volatile fractions). As the temperature of the column is gradually raised, TPH compounds are separated according to their boiling points as they migrate towards the end of the column onto the flame ionization detector. In the detector, the high-concentration effluent eluting the column are trapped and ionized by burning them in a hydrogen-air or oxygen flame causing the gas in the detector to conduct electric current, and the conductivity is measured by a DC-powered collector electrode above the flame. The retention time of a compound prior to elution from the column is typical of the species under a set of conditions and is used to correlate the detector response to the amount of compound present. The detector responses in a given range are then integrated to give the total concentration of hydrocarbons referral to external and/or internal hydrocarbon standards (31, 49).

GC/FID is mostly preferred for laboratory applications as they provide relative selectivity and sensitivity (18, 31–33), and is recognised by the USEPA, BSI and ISO. The EPA Method 8015 is to be used to determine TPH, BS ISO 15009:2002 is for volatile aromatic and halogenated hydrocarbons, and BS ISO 16703:2004 is for the determination of content of hydrocarbons in the range C$_{10}$ to C$_{40}$ (n-alkanes), from solids including soils and wastes (50–53). GC/FID is used for both quantitative and qualitative applications including the screening of environmental samples (54–56), unravelling the type and identity of fresh to mildly weathered oil in environmental samples for pattern recognition of the petroleum hydrocarbons (18, 19), and characterising and resolving the profile of unresolved complex mixtures (UCM) in petroleum-contaminated sediments (57). The biodegradation rate constant of petroleum-hydrocarbons in a contaminated site is highly variable and difficult to evaluate due to variable site conditions. But, GC/FID has been used to develop a simple correlation.
model to estimate the bioventing degradation rate constant of gasoline in several soils without having to conduct lengthy and expensive experiments (58). Detection limits for GC/FID depend on the method and sample matrix with typical values of 10 mg/kg in soil (31). However, high analytical costs and operational time (21, 59), instrument calibration problems (60), effects of sample matrix (56), and impact of GC operating conditions (61) are some of the challenges of the method (see also Table 3).

2.1.4. Gas Chromatography/Mass Spectrometry (GC/MS)

Over the years, a couple of alternative detection techniques to the FID (Table 1) have been developed for more detailed analysis of a wider range of sample matrix due to the selectivity of the FID for hydrocarbons (32). The most prominently used is the mass spectrometric detection (MSD) technique. The MSD basically uses the characteristic mass spectra of molecular and/or fragmented ions produced after ion impact to identify compounds in the sample (62). The mass spectrometer has been described as a universal detector because of its versatility in the measurement of TPH, PAHs and the compound specific biomarkers (CSB) for a wide variety of environmental samples (63), and is recommended by the USEPA for the determination of both TPHs and PAHs (EPA Methods 8270 and 625). The popular choice of mass selective detector for most environmental analysis is because of its specificity and discrete monitoring capabilities; particularly when operated in the selective-ion mode (63). As part of its wide-reaching application, GC/MS has been used in environmental monitoring programmes to assess sediment quality in terms of concentration of total PAHs (64), to investigate the amount of PAHs in the topsoil of a tar-contaminated industrial site (65), for the fingerprinting analysis of some environmental sediments containing unsaturated priority PAHs [66], and to monitor the bioremediation of PAH-contaminated soil through in-vessel composting with fresh organic wastes (67). But, despite its widespread application, a
major drawback of the GC/MS is that it requires volatile and thermally stable analytes; as such, only about 10% of organics are amenable to GC/MS analysis (68). More so, the MSD is reported to have a lower sensitivity than the FID, because in the impact ion mode, the respective detectors collect and measure different proportions of the generated molecular ions (63). Quantitative chemical analysis with laboratory-based GC/MS is undoubtedly very exhaustive but, like the GC/FID, involves lengthy and labour-intensive extraction protocols, costly GC-based analysis, and is uneconomical in the assessment of large-scale contamination involving dense sampling for mapping of zones requiring remediation (64).

2.2. Field-based techniques

2.2.1. Immunoassays (IMA)

IMA is a field-based immunochemical method in which antibodies are used to selectively bind specific petroleum constituents (31). The underlying principle of the IMA methods is variable; depending on the linked label used for response detection. The most prominent are: enzyme-linked immunosorbent assay (ELISA), fluorescence immunoassay and electrochemical immunoassay (ECIA).

In the ELISA method, the response of an antibody to sorb the sample analyte in relation to the enzyme-labelled analyte is determined by its optical density at sorption equilibrium. The concentration of the analyte in the sample is inversely related to the optical density of the antibody since the labelled enzyme, with high antibody affinity, is more sensitive to the colouring agent (31). Currently, there are a number of commercially available ELISA test kits including Ensys™ and RaPID™ assay (Strategic Diagnostics Newark, USA). Ensys™ is less sensitive to heavier hydrocarbon components usually found in weathered oils (45). RaPID™ assay has been used for the measurement of polycyclic aromatic hydrocarbons (PAHs) in soil (68) and electrical transformer oil (69) but, according to a recent study (70), is
prone to the problem of cross-reactivity. Cross-reactivity, which is the ability to respond to compounds structurally similar to the analyte, affects the specificity of PAH immunoassays and often results in biased results because PAHs are a class of structurally related compounds (70). As a result, the ELISA test kits are unsuitable for risk-based studies, which involve the assessment of PAHs in the medium. They are, however, recognised by the USEPA as official screening methods for TPH (EPA Method 4030) and PAHs (EPA Method 4035).

Fluorescence immunoassay is based on selective antigen-antibody binding and fluorescence label reagents (31) and its use for the screening of aromatics in mainly water samples is widespread (45). Regardless of the media, it is important to note that fluorescence immunoassay also suffers the same cross-reactivity problems as the ELISA test kits as reports show that about 15% cross-reactivities of the anti-Naphthalene antibody bound to seven structurally related compounds are observed during the screening of Naphthalene in water samples with fluorescence immunoassay (29). This problem is even more complex in real-world situation since potential cross-reactants are unlimited in number and most are seldom determinable; so all cross-reactivity values for the cross-reactants for PAH immunoassays is all too difficult to determine (70).

Redox-labelled electrochemical immunoassay (ECIA) is a direct competitive immunoassay based on surface-immobilized anti-PAH monoclonal antibody and electro-catalytic redox-labelled tracer recently developed for Benzo[α]pyrene measurement (30). Although, detection limit of a 2.4 ng/mL was reported, it has been observed not sufficient for most practical applications. Additionally, cross-reactivity is not peculiar to polyclonal immunoassays but, is also a major challenge for monoclonal immunoassays (70) including redox-labelled ECIA; suggesting that ECIA also suffers the same fate as both ELISA test kits and fluorescence immunoassay. On top of these, it has been reported that immunoassay test
methods are affected by soil matrix, age of weathered oil, and that their sensitivity to hydrocarbons decreases with increasing soil clay content (31).

2.2.2. Fluorescence spectroscopy

Fluorescence spectroscopy is a spectrochemical method of analysis in which the molecules of the analyte emit longer wavelength radiation in less than a microsecond during the process of relaxation to lower energy after excitation (Figure 1) by an incident shorter wavelength radiation.

Qualitative and quantitative information about the analyte is provided by the characteristic emission spectrum produced (71). It is a field portable technique that has been used to detect fluorescent compounds like the PAHs based on the principle that the intensity of the emitted radiation is indicative of the relative concentration of the PAH as well as the number of aromatic rings. Petroleum hydrocarbon molecules absorb energy in the wavelength range of 200 to 400 nm and fluoresce in the range 280 to 500 nm with each molecule fluorescing at a specific wavelength thereby enabling the possibility of differentiating between the various molecular classes (72). Monocyclic aromatic hydrocarbons (MAHs) fluoresce at lower wavelengths than the PAHs whereas the lower boiling PAHs such as Naphthalene fluoresce at lower wavelengths than the higher boiling PAHs like Benzo[a]pyrene (72). Some commonly used fluorescence spectroscopic methods include the ultraviolet-induced fluorescence (UVIF) and Rapid Optical Screening Tool (ROST™) laser-induced fluorescence (LIF).

The UVIF employs a powerful UV lamp, which energises the hydrocarbons on illumination thereby causing them to fluoresce. The fluorescence signal is detected with a charge coupled device (CCD) camera, a polychromator (or a combination of both) or a silicon intensified target (SIT) camera. Most application utilise cone penetrometer technology.
(CPT). The CPT enables continuous measurement over the subsurface media of the investigation; providing semi-quantitative measurements (22). In one report, the United States Environmental Protection Agency (USEPA) has reported an average analysis time of 2.6 minutes and a detection limit of 3.4 mg/kg for field TPH measurement with the UVF-3100A device (73). Using the QED™ hydrocarbon analyser designed by QROS®, even lower detection limits of 1 mg/kg in soils for petroleum fuels and oils and 0.1 mg/kg for PAHs in soil can be achieved in a single 5-second analysis with a throughput capacity of up to 15 samples per hour (72). Currently, in the US state of North Carolina, the QED™ hydrocarbon analyser has been approved as a replacement for the USEPA method 8015 (based on GC/FID) for monitoring remediation of fuel spills from Leaking Underground Storage Tanks (LUST) (72). Despite the quantitative strength of the UVIF, analysis of complex samples can be difficult due to overlap of spectra of different luminescent compounds, and prior sample extraction is required (22).

The ROST™ LIF system is a tunable dye laser-induced fluorescence system designed as a field screening tool for detecting petroleum hydrocarbons in the subsurface (74). Unlike the UVIF, the ROST™ LIF system uses a pulsed laser to cause fluorescence in PAH compounds instead of UV light. The laser is transmitted through a lorry-mounted CPT probe (housing a sapphire window) via excitation and emission optical fibres that are pushed into the ground (74). Available TPH data showed that the ROST™ LIF system can achieve an accuracy of 89.2% with false negatives and positives put at 5.4% respectively, and a limit of detection (LOD) of 5 mg/kg in soil (74). However, using PLS regression analysis, Aldstadt et al (71) reported sufficiently close match between predicted and measured PAHs for the technique to be used as a screening tool for all but 3 (i.e. Acenaphthylene, Dibenzo[a,h]Anthracen and Naphthalene) of the 16 priority PAHs. The ROST™ LIF system is designed for qualitative applications as it can only detect the presence or absence or relative concentration of
contaminants, sensitive to non-hydrocarbon compounds in the soil, and its sensitivity is
affected by soil matrix (22).

2.2.3. Field portable gas chromatograph/mass spectrometry (GC/MS)

Prompted by the need to reduce costly delays associated with laboratory-based GC
systems, their portable version is emerging. Currently, a variety of portable GC/MS systems
exist including (among others) CT-1128 GC-MS (Constellation Technology Corp., USA),
HAPSITE (INFICON, USA), and EM 640 (Bruker Instruments, USA). Reported average
weight of the portable GC systems is between 16 and 60 kg and typical analysis run time is
less than 10 minutes for some models (75). The field portable GC/MS systems obviously
differ from their laboratory-based counterparts (discussed later) in terms of provision of real-
time quantification. They however, require prior sample extraction, on-site carrier gas,
considerable electrical power and ancillary equipment just like the laboratory-based GC
systems (22). Some analysts have also observed that the major problem with existing portable
GC and GC/MS instruments, especially the microchip GCs, is sensitivity (75). A trade off
appears to exist between the size and performance of the GC/MS instruments such that the
smaller the portable GC or GC/MS instrument are, the greater the sacrifice in sensitivity,
separating power, and identifying power (75). Thus, according to Harris (75), there will
always be a place for the bench-top instrument for routine high-throughput, high-volume
analysis.

2.2.4. Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy based on the inelastic scattering (Anti
Stokes) of a monochromatic light source (Figure 2), usually from a laser source, used in
assessing the vibration of Raman-active molecules such as the PAHs and for identifying
species.

The Raman signal is detected with a charge coupled device (CCD) camera. Applications
of Raman spectroscopy have been widely reviewed (76), and Raman spectral data for several
PAHs have also been widely reported (77). In general, Raman spectroscopy is one of the
RMTs that have made it possible to obtain high quality spectra on a time scale that is
economical for analytical work (77). It suffices to say that Raman is both qualitative (78) and
quantitative (79) in its application. However, extreme care is needed to avoid laser alteration
of samples (80), and fluorescence contamination is often a problem with some Raman-based
systems (79). More so, in all Raman instrument, noise is present to some extent and is a
limiting factor in detection since it defines the detection limit of a particular compound (81).
It has also been observed that although the miniaturisation of the Raman instrument enhances
convenience, this has often come at a price as sensitivity; spectral range and spectral
resolution are sacrificed with possible negative consequences to materials identification and
verification (81).

2.2.5. Visible and near-infrared (vis-NIR) spectroscopy

The historical perspectives, fundamental principles and practical applications of NIR
spectroscopy have been widely reported in the literatures (82). In NIR spectroscopy,
absorption of energy by substances is due to overtones and combinations of fundamental
vibrations that occur in the mid infrared range (MIR) based on the stretching and bending of
bonds involving hydrogen and other atoms such as C-H, O-H, N-H and S-H chemical bonds
(82). Although, much of the early applications of NIR spectroscopy were for qualitative
purposes in the foods and beverages industry (82), its earliest qualitative and quantitative
applications in soil science predominantly for agricultural purposes were reported in the
Towards the end of the same period, the spectral characteristics of hydrocarbons were reported by Cloutis (84). The spectra of hydrocarbons originate mainly from combinations or overtones of C-H stretching modes of saturated CH$_2$ and terminal CH$_3$, or aromatic C-H functional groups (44).

For the purpose of this study however, only the quantitative cases regarding detection of TPHs and PAHs in soils are reviewed. A comprehensive review of non-invasive NIR spectroscopy involving several other processes and matrixes can be found in Workman (85) and Schwartz et al. (86). Following Cloutis’ work, by mid-1990’s a fibre-optic NIR reflectance sensor for the detection of organics, such as Benzene and Toluene, in soils has been developed and tested (87). Consolidating on the outcome of those investigations, albeit reportedly dismal, a small-scale study was initiated to investigate the applicability of reflectance spectroscopy (1600–1900 nm) on sandy loam artificially contaminated with motor oil (88). Two years later, a relatively more comprehensive study was conducted involving three soil types artificially contaminated with diesel and gasoline with reported minimum detection limits of 0.1 and 0.5 % by weight respectively (89). Away from the norm, Malley et al. (25) for the first time used NIR reflectance spectroscopy (1100–2498 nm) and the stepwise multiple linear regression to predict concentrations of TPH in diesel-contaminated soils collected from the field with low accuracy and high prediction error (Table 4). This low performance was attributed to the small number of sample set used and the inconsistency in the reference laboratory results (among others). A decade later, using different calibration models, Chakraborty et al. (26) reported fair TPH validation $R^2$ for field-collected intact soils from oil-spill sites with vis-NIR reflectance spectroscopy (Table 4). They acknowledged that small number of sample set resulted in the failure to develop robust calibration models. The possibility of using vis-NIR spectroscopy (400-2500 nm) in reflectance mode as a RMT for TPH in crude oil- and diesel-spiked soil minerals (kaolinite,
illite, smectite, carbonate and quartz) has also been reported by Forrester et al. (27) with relatively high calibration errors for some of the minerals (Table 4). Bray et al. (28) used an ordinal logistic regression technique for total PAH and benzo[a]pyrene predictions using vis-NIR spectroscopy with good accuracy and moderate to high false positive rate at low and high total PAH threshold respectively (Table 4). These results were attributed to a lack of samples. In 2012, three studies were reported (90 – 92) utilising laboratory-constructed hydrocarbon contaminated soil samples. Using several multivariate techniques and slightly higher number of sample set, Chakraborty et al. (90) predicted with significantly improved accuracy the amount of petroleum contamination in soil samples with vis-NIR spectroscopic method (Table 4). Schwartz et al. (91) employed several petroleum hydrocarbons (PHCs) for the simulated contamination of a total of 750 soil samples and used vis-NIR spectroscopic method to predict their TPH levels using PLS with unsatisfactory accuracy but good correlation results; a development they also attributed to the confirmed inter- and intra-laboratory inconsistencies in reference TPH results. The third study predicted PAHs in sets of artificially contaminated soils with vis-NIR diffuse reflectance spectroscopy (the second study on PAH to be reported in two years) with reported reasonably high accuracy levels as shown in Table 4 (92).

It must be pointed out, however, that the interaction of NIR radiation with soil sample produces soil spectra with fewer absorption features due to weak vibrational modes of molecular functional groups, broad and overlapping bands, which make NIR spectra difficult to interpret (93). This is besides the long pathlength of probe, which may decrease resolution and accuracy of the vis-NIR spectroscopic method. However, intensive research is being conducted today to improve the accuracy of vis-NIR spectroscopy.
3. Integration, analysis and discussion

When comparing technologies for the analysis of TPH and/or PAH in contaminated soils, several important attributes of general applicability can be used. In this review, the attributes discussed include economic considerations, operational time, occupational health and safety, portability and accuracy.

3.1. Economic considerations

The current capital equipment cost of different TPH and/or PAH analytical devices are shown in Table 2, which shows that the laboratory-based GC systems appear to be the most expensive probably due to their size and sophistication. Although the capital equipment cost of the portable EM 640 system is relatively on the high side, the capital equipment cost of the bench-top zNose™ 4200 or portable 3000 Micro GC 1-, 2-channel systems is comparatively low (Table 2). The capital cost of the NIR-based systems is much lower than the laboratory-based GC systems and portable EM 640 model. It is about the same range as the portable IR-based system, and ExoScan 4100, but higher than those of IMA, fluorescence, portable Raman spectroscopic and GC-MS systems (Table 2). In terms of analytical cost, a standard PAH or TPH analysis by GC-based method currently costs ~£100 per sample whereas the cost by the IR-based method is ~£32 per sample in a commercial laboratory in a developing country such as Nigeria, which is equivalent to the cost for a similar analysis in most developed countries like the United Kingdom (UK) way back in 2005 (21). Currently in the UK, it is possible that this cost may have increased considering the present economic realities. Analysts have always attributed this to the constantly increasing running cost of the GC-based systems. It is known that the analytical costs for most alternative methods, such as the FS-based systems, increase as the number of samples analysed decrease as a result of the spread of the initial capital equipment cost across the number of samples in contrast to the
fixed cost per sample of the reference laboratory methods (94). Consequently, the increase in the analytical cost per sample for such methods cannot be a fair comparison to the reference laboratory methods (94). For some other methods like the Raman and vis-NIR spectroscopic methods, their analytical costs are not well documented at the moment due to the absence of well-developed and standardised operating protocols, and cannot be fairly compared.

3.2. Operational time

Cycle time is the time it takes the analytical system to go from one analysis to the next (75), whereas analysis run time is the sum of the cycle time and the time spent preparing the sample for analysis. Sample preparation has got both occupational health (discussed later) and economic implications. During microcosm studies, experience shows that costly delays can result from overhead expenses due to high analysis run time. As shown in Table 3, high analysis run time is associated with techniques requiring lengthy initial sample preparation particularly the laboratory-based GC techniques; suggesting that the methods are uneconomical in the assessment of large-scale contamination involving dense sampling as has been previously reported (64). The portable GC systems can compare favourably with the non-invasive devices in terms of cycle time (Table 3) but, still involve time consuming sample extraction protocols. Although current data for gravimetric method were not available for comparison, the analysis run time for the laboratory-based IR, fluorescence spectroscopic and sorption-based IMA methods that which also require sample preparation, is comparable to those of the non-invasive Raman and NIR spectroscopic techniques. Table 3 shows that the portable IR, Raman and NIR spectroscopic techniques tend to have shorter analysis run time, since little or no sample preparation is required, as compared to those methods that depend on prior sample extraction. The shorter analysis run time of the portable IR, Raman and NIR spectroscopic techniques makes them potentially better techniques for cost-effective
assessment of large-scale contamination involving dense sampling, rapid decision making
and accurate contaminant mapping.

3.3. Occupational health and safety

As stated earlier, there are threatening occupational health and safety concerns associated
with sample preparation. Preparing samples for TPH and/or PAH analysis with the
gravimetric method [42, 43], IMA ELISA test kits (68, 95), laboratory-based IR spectroscopy
(47), fluorescence spectroscopy (73) and GC-based methods (19) obviously involves
handling of hydrocarbon-contaminated soil samples and noxious chlorinated extraction
solvents, which exposes the user to potentially biological and chemical hazards. For instance,
the solvent, tetrachloroethylene, often used as a substitute for Freon 113 for extracting TPH
compounds for analysis with laboratory-based IR spectroscopy is a potential carcinogen
according to the classification of the International Agency for Research on Cancer (IARC),
and is also a central nervous system depressant, which finds its way into the human body
through inhalation and skin contact (Wikipedia, The Free Encyclopedia). Similarly,
dichloromethane (DCM), a liquid extractant for TPH and PAH analysis by GC-FID or GC-
MS, and chloroform and toluene, liquid extractants for TPH analysis by gravimetric method,
all have serious health implications as evident in the risk phrases contained in their respective
safety data sheets. Other equally dangerous chemicals (liquid or powder), which come in
sealed bottles or bags that the operator must be exposed to when the containers are opened up
during the making up of standard solution mixes for GC-based analysis are PAH and TPH
calibration standards, internal standards such as deuterated alkanes and PAHs, and surrogate
spike standards such as Squalane, α-Terphenyl, 2-Fluorobiphenyl, Heptamethylnonane etc.

On the other hand, the portable IR devices such as the Agilent® 4100 ExoScan FTIR
(96), the vis-NIR devices, fluorescence devices such as the UVF 3100 (73) and Raman
devices employ electromagnetic radiation for property elucidation. In Raman spectroscopy, the electromagnetic radiation is capable of penetrating glass and plastic containers enabling in-vessel analysis thereby eliminating or reducing possible exposure to hazardous chemicals (97) but, operators still face possible exposure to fugitive lasers necessitating a Class 3B laser warning on the devices to comply with regulations. Even though the vis-NIR and portable IR devices employ particle physics in their applications, which eliminates the need for a liquid extractant and concomitant exposure to chemical hazard, there is still a need, according to their data sheets, for a close proximity between the sample and the detectors for better instrument sensitivities. This implies that possible contact with the contaminated soil sample and exposure to both biological and unknown hazards cannot be completely eliminated. In the same vein, fluorescence spectroscopy employing CCD (charge-coupled device) camera may still pose a radiation risk to the operator in addition to exposure to different proprietary extraction and calibration solvents often used during sample preparation.

3.4. Portability

Considering recent innovations, it appears that there is no clear-cut distinction between field- and laboratory-based techniques. Some techniques such as those based on IR, Raman and fluorescence spectroscopies, and the GC-based techniques, which are laboratory-based, are now also available in manageable sizes that can be deployed for field measurements and are now more user friendly (Table 3). For examples, with the coming on stream of the portable GC-MS devices (Table 3), and the portable IR systems such as the Agilent 4100 ExoScan FTIR (96) difficult circumstances can now be accessed in situ with relative ease. To the best of our knowledge, apart from the gravimetric methods, virtually all the techniques now come in field-implementable devices essentially for convenience and to also assuage the cost on logistics. However, it has been reported that miniaturisation of the GC-MS (75) and
Raman (81) devices results in loss of instrument performance. However, we were not able to ascertain if this problem also affects the IR- and IMA-based techniques as well as the fluorescence and vis-NIR spectroscopic techniques. Field-portable devices in general, apart from being cost-effective, simple and easy to use, are meant to reduce the amount of time spent in conventional laboratory-based analysis, expedite the screening of contaminated sites to pave the way, if need be, for more detailed investigation (36).

3.5. Accuracy

More often than not, the performance of the standard analytical techniques is used as a benchmark for the innovative techniques because they are assumed to be very accurate when compared to the innovative methods. Consequently, the innovative techniques are seen to play a complementary role to the standard analytical techniques, and more so, as their data ultimately will have to be verified by the relevant standard analytical techniques such as the GC, IR spectroscopy, and general gravimetry (Table 4). The accuracy of an innovative analytical technique relative to a standard analytical method can be determined using different indicators (98). Although the root mean square error is commonly used for estimating the performance of NIR and IR techniques, it was not possible to be adopted since this was not reported while estimating the accuracy of other methods discussed in this report. The correlation coefficient, $R^2$, value is seen in this report as the common denominator among other indicators so far reported by previous researchers (Table 4) and was, therefore, used to fairly compare how good or badly a particular innovative technique has been able to predict TPH and/or PAH values relative to a chosen standard analytical method. For a fair comparison, though, average values of $R^2$ were used, and for the vis-NIR technique, only validated values, $R^2_p$, were used (see Table 4). We assumed a $R^2$ value between 0.9 and 1.0 as an excellent correlation, $R^2$ value between 0.8 and 0.89 to be a good correlation, $R^2$ value
between 0.7 and 0.79 to be a fair correlation, and $R^2$ value between 0.5 and 0.69 as a poor correlation. Average values of $R^2$ deduced show that the fluorescence spectroscopic method performed best with the highest average $R^2$ value of 0.95, which implies an excellent correlation and suggests this technique to be the best to assess TPH and/or PAHs as compared to the other innovative techniques. This is followed successively by the IMA-based method (average $R^2 = 0.81$) and the vis-NIR method (average $R^2 = 0.78$), implying a good and fair performance respectively. Raman spectroscopic method could not be fairly compared because the standard analytical method used in the studies we accessed was either not stated or was the high performance liquid chromatography (HPLC), which is outside the scope of this review.

4. Overall performance and method-specific recommendations

Overall, Table 5 shows that most of the analytical techniques compare very well with fluorescence spectroscopy topping the table, while the gravimetric method made it to the bottom of the table. Fluorescence spectroscopy has excellent records in 60% of the attributes but, a good operational time and a fair occupational health and safety records (Table 5), which suggest that improvements should be geared towards reducing or completely eliminating the need for prior sample preparation.

The IMA evidently is economical, portable and has good accuracy but, has only a fair record for operational time and health and safety issues (Table 5) due to dependence on solvent extraction. So, like every other solvent extraction-dependent method, the IMA would require (among others) an operating protocol that will be less dependent on, or independent of, chlorinated extraction solvents. Although the GC-based method has 65% in the overall assessment, its high accuracy is well depicted in Table 5. This low overall score obviously is not unconnected with the effects of the poor health and safety records and the fair economic
and operational time factors. The portable GC/MS systems undoubtedly had a positive influence on the mobility of the method. However, the introduction of the portable GC/MS devices did not have much positive impact on the economic (based on capital equipment cost), operational time and health and safety concerns of the method. This is because the cost of most portable GC/MS devices is still relatively high (Table 5), and the method is still reliant on time consuming extraction protocols and the use of extraction solvents. Therefore, operating protocols that encourage the use of non-chlorinated solvents without compromising analyte recovery may well improve on its health and safety impacts, while instrument design that eliminates completely the need for prior sample extraction will definitely enhance timeliness. The gravimetric method is cheap and has an assumed excellent accuracy record, because it is assumed that standard methods are reference frames against which innovative methods are referred. But, this is a laboratory-based method with poor health and safety records and a fair operational time (Table 5) due to the extraction step involved. Therefore, the gravimetric method would require the same improvement recommended for other extraction-dependent analytical methods earlier stated.

The IR and vis-NIR spectroscopies performed equally well on the overall score sheet (Table 5). The significantly improved records of the IR spectroscopy may be attributed to the enhanced accuracy and portability of the method brought about by the introduction of the portable IR devices. On the other hand, the vis-NIR spectroscopy has excellent records in terms of portability and operational time, and good records in economic and health and safety standpoints (Table 5). However, the vis-NIR spectroscopy has only a fair accuracy record, which appears to be the least among other methods (Table 5). The reason for this is that NIR prediction is based on overtones and combinations of fundamental vibrations occurring in the mid IR region. Therefore, significant improvement on the accuracy of the vis-NIR spectroscopy is required. Possible solutions may include: the use of non-linear multivariate
analytical methods such as artificial neural networks (ANN) as an alternative to PLS regression analysis, and understanding the effects of other affecting parameters (e.g. soil texture, moisture content and oil concentration) on soil diffuse reflectance spectra of contaminated soils. Soil properties have been predicted with higher accuracy with the ANN than the PLS regression analysis with the vis-NIR spectroscopy (99). Similarly, Mouazen et al. (100) and Mouazen et al. (101) have reported that soil texture and moisture content respectively, negatively affect the performance of NIR spectroscopy in the prediction of soil chemical properties. By sufficiently understanding the individual and combined effects of these three factors, it is expected to establish techniques to reduce or even eliminate the effects of these factors and thus lead to improved accuracy of calibration models developed to predict TPH and/or PAHs in petroleum hydrocarbon-contaminated soils. Laboratory- and field-scale studies to address these key areas are being undertaken by the authors.

4. Conclusions

On a regular basis, analytical techniques for TPH and/or PAHs in soils are being developed and diverse factors are coalescing to bring this about. Top on this list of factors is the increasingly persistent demand for more profitable and simple environmental diagnostic tools capable of generating reliable data on a time scale. From this study, it is obvious that there is seldom an analytical technique that is problem-free although, some are less problematic than others. This is why efforts have been made in this study to extract as much relevant information from the open access literature as possible on the application of vis-NIR spectroscopy in particular, and analytical techniques in general, in the detection of petroleum contamination in soils. If timeliness and operator health and safety are anything to go by, improved protocols aimed at completely eliminating the need for prior sample preparation and the use of chlorinated extraction solvents become a consequent tandem. This suggested
method change should necessarily target the gravimetric, GC-based, IMA-based, and fluorescence spectroscopic techniques because of their low performance in those two attributes due to their dependence on lengthy sample preparation steps involving the use of chlorinated extraction solvents and proprietary extraction kits. Although the vis-NIR technique compares well with other techniques in terms of cost-effectiveness, timeliness, operator health and safety and portability, it was documented to be the least accurate. This has to do with the fact that NIR prediction is based on overtones and combinations of fundamental vibrations occurring in the mid IR region. However, if the individual and interaction effects of soil texture, moisture content and oil concentration on soil diffuse reflectance spectra and calibration models developed are well understood, and if non-linear analytical techniques such as the artificial neural network (ANN) or support vector machine (SVM) and others could be applied as alternatives to linear PLS regression analysis used so far in the literature, the accuracy of the method may be improved. These are pertinent research questions that need to be answered.

To this end, there always will be room for some breakthroughs in trying to improve on existing systems by scientists, and for some techniques to complement others. Therefore, there is a need for constant reviews of the progress being made to help scientists avoid duplicating efforts by re-inventing the wheel.

Acknowledgements

The authors are grateful to the Petroleum Technology Development Fund (PTDF), Nigeria, for funding this research through financial assistance in the form of doctoral studentship.

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Table 1: Summary of selected spectroscopic and non-spectroscopic techniques for petroleum hydrocarbon measurement (modified with permission from Reference (31))

Table 2: Capital cost of selected total petroleum and polycyclic aromatic hydrocarbon analytical devices (as of 2012; from the below companies †)

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Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils

Table 5: Attributes of general applicability for selected analytical methods for total petroleum and polycyclic aromatic hydrocarbons in soil
Table 1: Summary of selected spectroscopic and non-spectroscopic techniques for petroleum hydrocarbon measurement (modified with permission from Reference (31))

<table>
<thead>
<tr>
<th>Measurement technique</th>
<th>Detection device</th>
<th>Measured Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatography</td>
<td>Flame ionisation detector (FID)</td>
<td>TPH</td>
</tr>
<tr>
<td></td>
<td>Mass spectrometry (MS)</td>
<td>TPH, PAH and CSB</td>
</tr>
<tr>
<td>Infrared Spectroscopy</td>
<td>IR spectrometer</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td>General Gravimetry</td>
<td>Gravimetric balance</td>
<td>TPH</td>
</tr>
<tr>
<td>Immunoassay</td>
<td>ELISA kits</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td></td>
<td>ECIA kits</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>CCD detector</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td>Fluorescence Spectroscopy</td>
<td>Polychromator / CCD camera</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td></td>
<td>SIT camera</td>
<td>TPH and PAH</td>
</tr>
<tr>
<td>Visible and Near-infrared</td>
<td>High intensity probe / Mug lamp</td>
<td>TPH and PAH</td>
</tr>
</tbody>
</table>

CCD, Charge-coupled device
CSB, Compound specific biomarkers
ECIA, Electrochemical immunoassay
ELISA, Enzyme-linked immunosorbent assay
PAH, Polycyclic aromatic hydrocarbon
SIT – Silicon intensified target
TPH, Total petroleum hydrocarbon
Table 2: Capital cost of selected total petroleum and polycyclic aromatic hydrocarbon analytical devices (as of 2012; from the below companies†)

<table>
<thead>
<tr>
<th>Technique</th>
<th>Make</th>
<th>Model</th>
<th>Price ($) (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatography</td>
<td>Agilent Technologies</td>
<td>6890 N GC/FID</td>
<td>28,000 (used)</td>
</tr>
<tr>
<td></td>
<td>Agilent Technologies</td>
<td>GC/MS 6890/5975</td>
<td>39,900 (used)</td>
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<tr>
<td></td>
<td>Thermo Fisher</td>
<td>LTQ Orbitrap</td>
<td>362,486</td>
</tr>
<tr>
<td></td>
<td>Agilent Technologies</td>
<td>3000 Micro GC 1-, 2-channel systems (portable)</td>
<td>17,000–50,000</td>
</tr>
<tr>
<td></td>
<td>zNose™</td>
<td>Model 4200 (bench-top)</td>
<td>21,000–26,000</td>
</tr>
<tr>
<td></td>
<td>Bruker Instruments</td>
<td>EM 640 (portable)</td>
<td>149,530–175,375</td>
</tr>
<tr>
<td>Infrared Spectroscopy</td>
<td>Shimadzu</td>
<td>IR400</td>
<td>3,528</td>
</tr>
<tr>
<td></td>
<td>Thermo Fisher</td>
<td>370 DTGS</td>
<td>7,055</td>
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<tr>
<td></td>
<td>Thermo Scientific</td>
<td>Nicolet 6700 FTIR</td>
<td>14,900 (used)</td>
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<td></td>
<td>Agilent Technologies</td>
<td>4100 ExoScan FTIR (Diffuse Reflectance Head)</td>
<td>43,497</td>
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<td></td>
<td>Agilent Technologies</td>
<td>4100 ExoScan FTIR (Universal System)</td>
<td>61,301</td>
</tr>
<tr>
<td>Immunoassay</td>
<td>Pierce</td>
<td>Easy Titer ELISA Systems</td>
<td>546</td>
</tr>
</tbody>
</table>

†LabX, Canada; Analytik Ltd., UK; O. I. Analytical Corp., USA; StellarNet Inc., USA
Table 2: Capital cost of selected total petroleum and polycyclic aromatic hydrocarbon analytical devices (as of 2012; from the below companies †)

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<th>Technique</th>
<th>Make</th>
<th>Model</th>
<th>Price ($) (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visible and Near-infrared Spectroscopy</td>
<td>Analytical Spectral Devices</td>
<td>Quality-SpecPro®</td>
<td>48,563</td>
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<td></td>
<td></td>
<td>LabSpec®2500</td>
<td>56,688</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LabSpec®5000</td>
<td>61,078</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Hitachi</td>
<td>F-4010</td>
<td>2,500</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>Tecan</td>
<td>Spectra Fluor</td>
<td>8,200</td>
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<tr>
<td></td>
<td>Perkin Elmer</td>
<td>LS5B</td>
<td>4,500</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>-</td>
<td>Raman-HR-TEC-IG</td>
<td>17,777</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Raman-HR-TEC</td>
<td>5,295</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Raman-HR</td>
<td>4,000</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Raman-SR</td>
<td>3,500</td>
</tr>
</tbody>
</table>

†LabX, Canada; Analytik Ltd., UK; O. I. Analytical Corp., USA; StellarNet Inc., USA
Table 3: Characteristics of selected petroleum hydrocarbon measurement techniques (modified with permission from Reference (31))

<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Approx. LDL (mg/kg)</th>
<th>Estimated analysis run time (minutes)</th>
<th>Sampling type</th>
<th>Strength</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC-Based</td>
<td>Laboratory and field</td>
<td>10</td>
<td>45 – 2880 (^{b,c})</td>
<td>Purge &amp; trap,</td>
<td>Selectivity and high sensitivity; oil source identification; specific</td>
<td>Laboratory-based GCs are not for compounds &lt; C6; Non-specific (FID); specific</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Excluding extraction time, lab-based GC cycle may be 40 minutes while some portable devices take &lt;10 seconds)</td>
<td>Head-space, Solvent extraction (MSD); quantitative and qualitative applications, portable, rapid</td>
<td>(MSD); Expensive (capital equipment and analytical costs); Problem of co-elution; expensive; requires expertise; produces COPC</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) In soil

\(^{b}\) Reference (45)

\(^{c}\) Reference (21)

LDL, Laboratory detection limit

COPC, Constituents of potential concern
Table 3: Characteristics of selected petroleum hydrocarbon measurement techniques (modified with permission from Reference (31)) Continued

<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Approx. LDL (mg/kg)</th>
<th>Estimated analysis run (minutes)</th>
<th>Sampling type</th>
<th>Strength</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR-Based</td>
<td>Laboratory and field</td>
<td>6.32 - 15.2</td>
<td>1 (Excluding sample extraction time for lab-based bench-top device)</td>
<td>Solvent</td>
<td>Quick, simple and inexpensive, portable</td>
<td>Non-specific; low sensitivity; analytical losses; poor extraction efficiency; quantitative application only; produces COPC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3 (No sample extraction required for the portable device)</td>
<td></td>
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<tr>
<td>Gravimetric</td>
<td>Laboratory</td>
<td>50</td>
<td></td>
<td>Solvent</td>
<td>Quick, simple and inexpensive</td>
<td>Non-specific; low sensitivity; analytical losses; poor extraction efficiency; quantitative application only; produces COPC</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
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</table>

*a In soil
*d Reference (73)
*j Reference (94)
*m Reference (96)
Table 3: Characteristics of selected petroleum hydrocarbon measurement techniques (modified with permission from Reference (31)) *Continued*

<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Approx. LDL (mg/kg) (^a)</th>
<th>Estimated analysis run (minutes) (^b)</th>
<th>Sampling type</th>
<th>Strength</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immunoassay</td>
<td>Field</td>
<td>10-500 (under laboratory conditions, 0.1 has been achieved with trained staff) (^c)</td>
<td>1.5 – 3 (^c)</td>
<td>Optical density</td>
<td>Quick, simple, inexpensive and portable; increasingly reasonable accuracy</td>
<td>Non-specific; low sensitivity; only measures aromatics; quantitative application; screening only, cross-reactivity</td>
</tr>
</tbody>
</table>

\(^a\) In soil

\(^b\) Dexsil, USA

\(^c\) Reference (68)

LDL, Laboratory detection limit
<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Approx. LDL (mg/kg)</th>
<th>Estimated analysis run time (minutes)</th>
<th>Sampling type</th>
<th>Strength</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIR-Based</td>
<td>Field</td>
<td>1.0&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.6&lt;sup&gt;g&lt;/sup&gt; – &lt; 2&lt;sup&gt;h&lt;/sup&gt;</td>
<td>Diffuse</td>
<td>Rapid, simple, inexpensive, portable, zero-solvent extraction, non-invasive, little or no sample preparation</td>
<td>Non-specific, matrix effect (water, soil &amp; nature of oil), overlapping spectra, long pathlength, indirect correlation, qualitative applications, high-level chemometrics</td>
</tr>
</tbody>
</table>

<sup>1</sup> Reference (25)

<sup>2</sup> Reference (23)

<sup>3</sup>Reference (25)

LDL, Laboratory detection limit
Table 3: Characteristics of selected petroleum hydrocarbon measurement techniques (modified with permission from Reference (31)) Continued

<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Approx. LDL (mg/kg)</th>
<th>Estimated analysis run (minutes)</th>
<th>Sampling type</th>
<th>Strength</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence-based</td>
<td>Laboratory</td>
<td>0.05&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Emission</td>
<td>Rapid, portable, specific, inexpensive, quantitative &amp; qualitative applications</td>
<td>Qualitative applications only, sensitive to non-hydrocarbons, sensitivity is affected by soil matrix, prior sample extraction is required</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>Laboratory</td>
<td>-</td>
<td>0.1&lt;sup&gt;i&lt;/sup&gt; – &lt; 3&lt;sup&gt;k&lt;/sup&gt;</td>
<td>Emission</td>
<td>Rapid, portable, non-invasive, inexpensive, quantitative &amp; qualitative application, specific</td>
<td>Laser alteration of samples, fluorescence contamination</td>
</tr>
<tr>
<td></td>
<td>and field</td>
<td></td>
<td></td>
<td>spectra</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> In soil  
<sup>d</sup> Reference (73)  
<sup>i</sup> DeltaNu, Inc., USA  
<sup>k</sup> Reference (101)  

LDL, Laboratory detection limit
Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils

<table>
<thead>
<tr>
<th>Innovative method</th>
<th>Reference method</th>
<th>Deployed</th>
<th>Measured target</th>
<th>Multivariate approach</th>
<th>No of samples</th>
<th>Spectral pre-processing</th>
<th>Wavelength range (nm)</th>
<th>Statistical parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMA-Based</td>
<td>GC-MS</td>
<td>Field</td>
<td>PAH</td>
<td>-</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>( R^2 (0.61-0.68) )</td>
<td>(68)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RSD (0.3-55 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( p )-value (&lt;0.001)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GC-MS</td>
<td>✓</td>
<td>PAH</td>
<td>-</td>
<td>11</td>
<td>-</td>
<td>-</td>
<td>( R^2 (0.94-0.99) )</td>
<td>(95)</td>
</tr>
<tr>
<td>FS-Based</td>
<td>GC-FID</td>
<td>Field</td>
<td>PAH</td>
<td>-</td>
<td>595</td>
<td>-</td>
<td>254</td>
<td>( R^2 (0.90-0.97) )</td>
<td>(73)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(For GRO→EDRO)</td>
<td></td>
</tr>
<tr>
<td>IR-S</td>
<td>✓</td>
<td>TPH</td>
<td>-</td>
<td>30</td>
<td>370-524</td>
<td>RSD (5-124 %)</td>
<td>(102)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-MS</td>
<td>✓</td>
<td>PAH</td>
<td>-</td>
<td>08</td>
<td>-</td>
<td>RSD (0.92)</td>
<td>(103)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC-MS</td>
<td>✓</td>
<td>PAH</td>
<td>-</td>
<td>Not stated</td>
<td>-</td>
<td>RSD (0.997)</td>
<td>(104)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vis-NIR</td>
<td>Not stated</td>
<td>Laboratory</td>
<td>Oil &amp; Grease</td>
<td>PLSR</td>
<td>17</td>
<td>1600-1900</td>
<td>SEP (0.13-0.26 %)</td>
<td>(88)</td>
<td></td>
</tr>
</tbody>
</table>

AVG – Average

URL: http://mc.manuscriptcentral.com/spectroscopy  Email: jsneddon@mcneese.edu
CV – Cross validation
EDRO – Extended diesel range organics
GRO – Gasoline range organics
IR-S – Infrared spectrometer
PAC – Polynuclear aromatic compound
PAH – Polycyclic aromatic hydrocarbon
PLSR – Partial least squares regression
RSD – Relative standard deviation (SD/AVG)
SD – Standard deviation
SEP – Standard error of prediction (in mg/kg)
Vis-NIR – Visible and Near-infrared
Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils (continued)

<table>
<thead>
<tr>
<th>Innovative method</th>
<th>Reference method</th>
<th>Deployed</th>
<th>Measured target</th>
<th>Multivariate approach</th>
<th>No of samples</th>
<th>Spectral pre-processing</th>
<th>Wavelength range (nm)</th>
<th>Statistical parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis-NIR spectroscopy</td>
<td>Not stated Laboratory and Field</td>
<td>Oil &amp; Grease</td>
<td>PLSR</td>
<td>&gt;25</td>
<td>Apparent absorbance, Kubelka-Munk transformation, Saunderson correction, Mean value centring, MSC</td>
<td>800-2700</td>
<td>$R^2_{cv}$ (0.968-0.998) (CV)</td>
<td>SEP (0.116-1.04) (CV)</td>
<td>Bias (-0.001-0.586)</td>
</tr>
<tr>
<td>GC-FID</td>
<td>✓</td>
<td>TPH</td>
<td>Stepwise</td>
<td>26</td>
<td>Wavelength average, First derivative, &amp; Smoothing splines</td>
<td>1100-2498</td>
<td>$R^2_p$ (0.68 - 0.72)</td>
<td>SEP (0.84- 1.00)</td>
<td>RPD (1.76- 1.82)</td>
</tr>
</tbody>
</table>
BRT – Boosted regression tree

FTIR – Fourier transform infrared spectroscopy

MLR – Multiple linear regressions

MSC – Multiplicative scatter correction

PLSR – Partial least squares regression

$R^2$ – Correlation coefficient (CV, cross validation; P, prediction)

RMSE – Root-mean-error (CV, cross validation; P, prediction, in mg/kg)

RPD – Residual prediction deviation = (SD/RMSEP)

SEP – Standard error of prediction (in mg/kg)

TPH – Total petroleum hydrocarbon

Vis-NIR – Visible and Near-infrared
Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils (continued)

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<tr>
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<th>Reference method</th>
<th>Deployed</th>
<th>Measured</th>
<th>Multivariate approach</th>
<th>No of samples</th>
<th>Spectral pre-processing</th>
<th>Wavelength range (nm)</th>
<th>Statistical parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis-NIR spectroscopy</td>
<td>Gravimetric</td>
<td>Laboratory and Field</td>
<td>TPH</td>
<td>PLSR, BRT</td>
<td>46</td>
<td>Parabolic splice, Wavelength average, First derivative, Second derivative, smoothing splines</td>
<td>350-2500</td>
<td>$R^2_{cv}$ (0.64-0.85)</td>
<td>(26)</td>
</tr>
</tbody>
</table>

AVG – Average
FNR – False negative rate
FPR – False positive rate
MLR – Multiple linear regressions
MSC – Multiplicative scatter correction

OLR – Ordinal logistic regression

PAH – Polycyclic aromatic hydrocarbon

PLSR – Partial least squares regression

$R^2$ – Correlation coefficient (CV, cross validation; P, prediction)

RMSE – Root-mean-error (CV, cross validation; P, prediction, in mg/kg)

RPD – Residual prediction deviation = (SD/RMSEP)

TPH – Total petroleum hydrocarbon

Vis-NIR – Visible and Near-infrared
Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils (continued)

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<th>Innovative method</th>
<th>Reference method</th>
<th>Deployed target</th>
<th>Measured</th>
<th>Multivariate approach</th>
<th>No of samples</th>
<th>Spectral pre-processing</th>
<th>Wavelength range (nm)</th>
<th>Statistical parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis-NIR spectroscopy</td>
<td>FTIR</td>
<td>✓</td>
<td>TPH</td>
<td>PLSR</td>
<td>172</td>
<td>Not reported</td>
<td>400-2500</td>
<td>$R^2_{cv}$ (0.81)</td>
<td>(27)</td>
</tr>
<tr>
<td>FTIR</td>
<td>✓</td>
<td>PAH</td>
<td>OLR</td>
<td>65</td>
<td>Not reported</td>
<td>350-2500</td>
<td>Accuracy (65.85-90.25%)</td>
<td>(28)</td>
<td></td>
</tr>
<tr>
<td>Not stated</td>
<td>Laboratory and Field</td>
<td>TPH</td>
<td>PLSR, MLR, Penalised Spline</td>
<td>68</td>
<td>First derivative, Discrete wavelet transform</td>
<td>350-2500</td>
<td>$R^2_{cv}$ (0.84-0.98)</td>
<td>(90)</td>
<td></td>
</tr>
</tbody>
</table>

MLR – Multiple linear regressions
PAH – Polycyclic aromatic hydrocarbon
PLSR – Partial least squares regression

URL: http://mc.manuscriptcentral.com/spectroscopy Email: jsneddon@mcneese.edu
R\(^2\) – Correlation coefficient (CV, cross validation; P, prediction)

RMSE – Root-mean-error (CV, cross validation; P, prediction, in mg/kg)

RPD – Residual prediction deviation = (SD/RMSEP)

TPH – Total petroleum hydrocarbon

Vis-NIR – Visible and Near-infrared
Table 4: Measurement accuracy of selected measurement techniques for petroleum hydrocarbons in contaminated soils (continued)

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<tr>
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<th>Wavelength range (nm)</th>
<th>Statistical parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vis-NIR spectroscopy</td>
<td>FTIR</td>
<td>✓</td>
<td>TPH</td>
<td>PLSR, ANN</td>
<td>750</td>
<td>SNV, MSC, Smoothing, first derivative, second derivative, continuum removal</td>
<td>Not stated</td>
<td>R² (0.79-0.99)</td>
<td>(91)</td>
</tr>
<tr>
<td>GC-MS</td>
<td>✓</td>
<td>PAH</td>
<td>PLSR</td>
<td>150</td>
<td>Noise cut, Wavelength average, Maximum normalisation, First derivative, Smoothing, Baseline correction</td>
<td>350-2500</td>
<td>R²cv (0.56-0.86)</td>
<td>(92)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>R²p (0.89)</td>
<td>RMSEP (0.201)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RMSECV (0.144-0.484)</td>
<td>RPD (1.52-2.79) (CV),</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.75(P)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AVG – Average
MLR – Multiple linear regressions
MSC – Multiplicative scatter correction
PAH – Polycyclic aromatic hydrocarbon
PLSR – Partial least squares regression
R² – Correlation coefficient (CV, cross validation; P, prediction)
RMSE – Root-mean-error (CV, cross validation; P, prediction, in mg/kg)
RPD – Residual prediction deviation = (SD/RMSEP)
SNV – Standard normal variate
TPH – Total petroleum hydrocarbon
Vis-NIR – Visible and Near-infrared
Table 5: Attributes of general applicability for selected analytical methods for total petroleum and polycyclic aromatic hydrocarbons in soil

<table>
<thead>
<tr>
<th>Method</th>
<th>Economic considerations †</th>
<th>Operational time</th>
<th>Occupational Health &amp; Safety</th>
<th>Portability</th>
<th>Accuracy ††</th>
<th>Overall score (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatography</td>
<td>××</td>
<td>××</td>
<td>×</td>
<td>××××</td>
<td>××××</td>
<td>65</td>
</tr>
<tr>
<td>Infrared Spectroscopy</td>
<td>×××</td>
<td>×××</td>
<td>×</td>
<td>×</td>
<td>××××</td>
<td>80</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>××××</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>××××</td>
<td>60</td>
</tr>
<tr>
<td>Immunoassay</td>
<td>××××</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>××××</td>
<td>75</td>
</tr>
<tr>
<td>Fluorescence Spectroscopy</td>
<td>××××</td>
<td>×××</td>
<td>×</td>
<td>×</td>
<td>××××</td>
<td>85</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>××××</td>
<td>×××</td>
<td>×</td>
<td>×××</td>
<td>-</td>
<td>Incomplete</td>
</tr>
<tr>
<td>Vis-NIR Spectroscopy</td>
<td>××××</td>
<td>×××</td>
<td>×</td>
<td>××××</td>
<td>×</td>
<td>80</td>
</tr>
</tbody>
</table>

× Poor

×× Fair

××× Good

×××× Excellent

† Based on capital equipment cost only for fair comparison
†† Note: the accuracy of the standard methods is assumed excellent since they are used as benchmarks for the innovative methods but, in practice this may not be so. The accuracy of the Raman spectroscopy could not be fairly compared because the standard analytical method used in the studies we accessed was either not stated or was the high performance liquid chromatography (HPLC), which is outside the scope of this review.
Figures

Figure 1: Electronic transition energy levels (Source: http://www.oswego.edu/~kadima/CHE425/CHE425L/FLUORESCENCE_SPECTROSCOPY_08.pdf)

Figure 2: Energy level diagram for Raman scattering process (Source: Wikipedia, The Free Encyclopaedia: http://en.wikipedia.org/wiki/Raman_spectroscopy). The line thickness is roughly proportional to the signal strength from the different transitions.
RE: Permission to use part of Table 4 (TPHCWG 1998, vol. 2)

FROM: Brenna Lockwood
TO: 'Reuben okparanma'
Message flagged
Wednesday, 14 December 2011, 14:52

Message Body

Reuben,

You have our permission to use the table for your review paper.

Thank you,

Brenna Lockwood
AEHS Foundation, Inc.
150 Fearing St., Suite 21
Amherst, MA 01002
413-549-5170 T
413-549-0579 F
brenna@aehsfoundation.org
www.aehsfoundation.org

From: Reuben okparanma [mailto:rokparanma@yahoo.com]
Sent: Tuesday, December 13, 2011 2:21 PM
To: orders@aehs.com
Subject: Permission to use part of Table 4 (TPHCWG 1998, vol. 2)

Dear Editor,

I am emailing to seek permission to use part of Table 4 in pages 20 and 21 in one of your publications: TPHCWG 1998, vol. 2, for a review paper intended to be submitted to the Environmental Science and Technology Journal.

Best wishes.

Reuben.

Reuben N. Okparanma,
Researcher, School of Applied Sciences,
 Cranfield University, Mk43 0AL Bedfordshire, UK.
rokparanma@cranfield.ac.uk
01234-750111 ext 2793