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Overview of Field-Based Analytical Techniques, Devices and Kits to Determine Petroleum Hydrocarbons in Soil

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Overview of Field-Based Analytical Techniques, Devices and Kits to Determine Petroleum Hydrocarbons in Soil

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ABSTRACT

Determination of petroleum hydrocarbons in soil has long been an area of active investigation and still attracting interest as there are important and complex environmental contaminants. Several standardised lab-based analytical techniques providing both accuracy and analytical precision are being used for their determination and quantification in soil. However, the procedures involved can be time-consuming and expensive, and therefore not always providing cost effective approaches to the assessment of sites contaminated with petroleum hydrocarbons.

Over the past decade, the emergence of various field analytical techniques has enabled real-time petroleum hydrocarbons detection and on-site measurement, which has the potential to drastically reduce cost and time of analysis, sampling design and site assessment compared with traditional technologies. In this review, we have designed and developed a practical guide on the use of field analytical technologies to rapidly assess petroleum hydrocarbons in soil. The basic principle along the advantages and limitations of each field analytical technique, and the recent developments over the past years, are highlighted.

The synthesis of information outlined in this review provides a firm foundation for an informed decision process in the selection of field analytical technologies for the detection and characterisation of petroleum hydrocarbons in soil.

KEYWORDS

Field analytical technologies; petroleum hydrocarbons; soil, site characterisation; real-time measurement; test kits; gas chromatography; spectroscopy; immunoassay; detectors.

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

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SUMMARY

This report describes the work undertaken on behalf of the Water, Soil & Waste Management Group of Concawe under the supervision of its Special Task Force on Soil and Groundwater (WQ/STF-33). The report provides an overview of the existing field-based techniques for the determination of petroleum hydrocarbons in soil.

Hydrocarbon compounds occur ubiquitously within the environment in the form of petroleum and its derivatives (so-called petroleum hydrocarbons) coal and its derivatives, and other naturally occurring organic materials. Given, the complex nature of petroleum hydrocarbon compounds, there is no single method that is suitable for determining all hydrocarbon compounds potentially present in the environment or in a sample. The result that is reported will depend upon the field analytical technologies used in the determination. The purpose of this report is therefore (1) to provide information that will facilitate the broader use of various field analytical technologies for the determination of petroleum hydrocarbons content in soil; (2) to provide a guidance on the selection of field analytical technologies during site investigation, remediation and validation activities, and (3) to encourage information exchange between various stakeholders on the key points and procedures to be considered for on-site petroleum hydrocarbons analytical technologies.

The field analytical kits and devices are classified according to detection methods, target analytes detected and data quality levels (qualitative, semi-quantitative and quantitative). For each analytical method and device or kit, a summary of performance, advantages and limitations is provided along with calibration and quality control requirements. Further to this, relative evaluation of the operator's skill level required to operate the device or kit, and ultimately, sample processing time and sample analysis cost, and equipment purchase cost are reported. A summary of the field analytical techniques criteria used to support selection is provided in **Table1**.

Overall, it was found that the approaches to field petroleum hydrocarbons measurement in current use represent mature, established technologies and recent advances have been incremental rather than fundamental. However, although generally well established, recent developments in field spectroscopic technologies show promise of allowing its wider application for real-time petroleum hydrocarbons measurements in soil such as supporting an on-the-go assessment which can inform an adaptative sampling design where sampling efforts are directed to areas where the degree of contamination appears to be higher.

Citation and inclusion of vendors as well as the use of trade names are for descriptive purposes only and should not be interpreted as any official or product endorsement.

Table 1: Overview of field analytical techniques criteria to support selection

Analytical technique	Instrument/ field test kit	Data Quality			Target compounds analysis				Operator skills	Sample processing time	Relative sample analysis cost
		Qual	Semi-Quant	Quant	VOC	BTEX	SVOC	PAH			
Gas chromatography coupled to mass spectrometry	HAPSITE®		👍	👍	◉	●	◔	●	🟥	🕓🟥	€🟥
	FLIR Griffin™ G510		👍	👍	◉	●	◔	●	🟥	🕓🟥	€🟥
	Torion T9 Perkin Elmer		👍	👍	◉	●	◔		🟥	🕓🟥	€🟥
	Environmental and BTEX GC SRI		👍	👍	◉	●			🟥	🕓🟥	€🟥
	Frog-5000		👍	👍	◉	●			🟥	🕓🟥	€🟧
Ionization	MicroFID II		👍		◉	●			🟧	🕓🟧	€🟩
	PID MiniRAE, RKI Eagle 2 FID		👍		◉	●			🟧	🕓🟧	€🟩
Spectroscopy	Infracal® TOG/TPH Analyser		👍	👍	◔		◉		🟩	🕓🟧	€🟧
	ASD FieldSpec 4 Hi-Res		👍	👍	◔		◉		🟥	🕓🟩	€🟩
	RemScan®		👍	👍	◔		◉		🟧	🕓🟩	€🟩
	4300 Agilent Handheld FTIR		👍	👍	◔		◉		🟥	🕓🟩	€🟩
	QualitySpec Trek		👍	👍			◉		🟧	🕓🟩	€🟩
	OCMA-350 Oil Content Analyser		👍	👍	◐		◐		🟧	🕓🟧	€🟧
Fluorescence	Analytical Test Kit UVF-3100A	👍	👍		◑		◑	●	🟧	🕓🟧	€🟧
	ROST®	👍	👍				◑		🟥	🕓🟥	N.A.
	SCAPS LIF	👍	👍		◑		◑		🟥	🕓🟥	N.A.
	TarGOST®	👍	👍				◑		🟥	🕓🟥	N.A.
	UV LED	👍	👍				◑		🟥	🕓🟥	N.A.
	UVOST®	👍	👍				◑		🟥	🕓🟥	N.A.
	DyeLIF™	👍	👍		◑		◑		🟥	🕓🟥	N.A.

Table 1 Cont'd

Analytical technique	Instrument/ field test kit	Data Quality			Target compounds analysis				Operator skills	Sample processing time	Relative sample analysis cost
		Qual	Semi-Quant	Quant	VOC	BTEX	SVOC	PAH			
Colorimetry	Hanby TPH Soil kit	👍	👍			●	⦶	●	👨‍🏫	🕒	€
	Dräger Detector Tubes	👍	👍		⦶	●			👨‍🏫	🕒	€
Immunoassay	RaPID® BTEX/TPH Assay	👍	👍		⦶	●			👨‍🏫	🕒	€
Turbidimetry	PetroFLAG® test kit	👍	👍		⦶		⦶		👨‍🏫	🕒	€

Key Table 1:
Qual: Qualitative; **Semi-Quant**: Semi Quantitative **Quant**: Quantitative;
VOC: Volatiles Organic Compounds - include a range of seleted low molecular weight aliphatic and aromatic hydrocarbons up to EC_{12}
BTEX: benzene, toluene, ethylbenzene and the three xylene isomers: a variant on VOC analysis which specifically targets BTEX
SVOC: Semi-volatiles Organic Compounds including aliphatic and aromatic hydrocarbons in the range of C_{12}-C_{40}
PAH: Polycyclic aromatic hydrocarbons: a variant of SVOC analysis targeted to the aromatic hydrocarbons group. This is usually the 16 PAHs listed in the US Environmental Protection Agency.
Target analytes:
⦶ Both aliphatic and aromatic hydrocarbons of the group
◐ Greater response towards aliphatic hydrocarbons.
◑ Greater response towards aromatic hydrocarbons.
◔ Covering only selected compounds ranges within the hydrocarbons group (i.e. spectroscopy only VOC between EC_{10}-EC_{12}; gas chromatography covering selected SVOC up to EC_{21})
Operator skill: 👨‍🏫 Low ; 👨‍🏫 Moderate 👨‍🏫 High;
Sampling processing time: 🕒 immediate (few sec); 🕒 intermediate (within few minutes); 🕒 long (several minutes);
Relative cost: € relatively low; € relatively moderate; € relatively high
N.A. Not applicable

1. INTRODUCTION

Several standardized lab-based analytical techniques are being used for the determination and quantification of petroleum hydrocarbons in soil. While these techniques provide accuracy and analytical precision, the procedures involved are time-consuming and can be expensive, depending on the number of samples and type of analysis to be conducted. Over the past decade, the emergence of various field analytical techniques, such as test kits and portable handheld devices, have enabled real-time petroleum hydrocarbons detection and measurement on-site, which has the potential to drastically reduce cost and time of analysis compared with traditional technologies (Kong et al., 2017), and without sacrificing 'Quality Management' objectives. Given the complex nature of petroleum hydrocarbons compounds, there is however no single method that is suitable for determining all hydrocarbon compounds potentially present in the environment or in a sample submitted to the laboratory. The result that is reported will depend upon the method used in the determination. Therefore, selecting which field analytical technology is suitable for a specific site, is an imperative process. It is also important to understand the type and quality of data that will be generated by field analytical technologies and interpretation of the data generated should be carefully evaluated before conclusions are drawn. Depending on which analytical technology is used, it is possible to achieve qualitative, semi-quantitative and quantitative results. In some cases, the accuracy of field analytical technology is approaching that achievable previously only from laboratory analysis. Yet, laboratory analysis may still be required in order to attain legally recognised measurements.

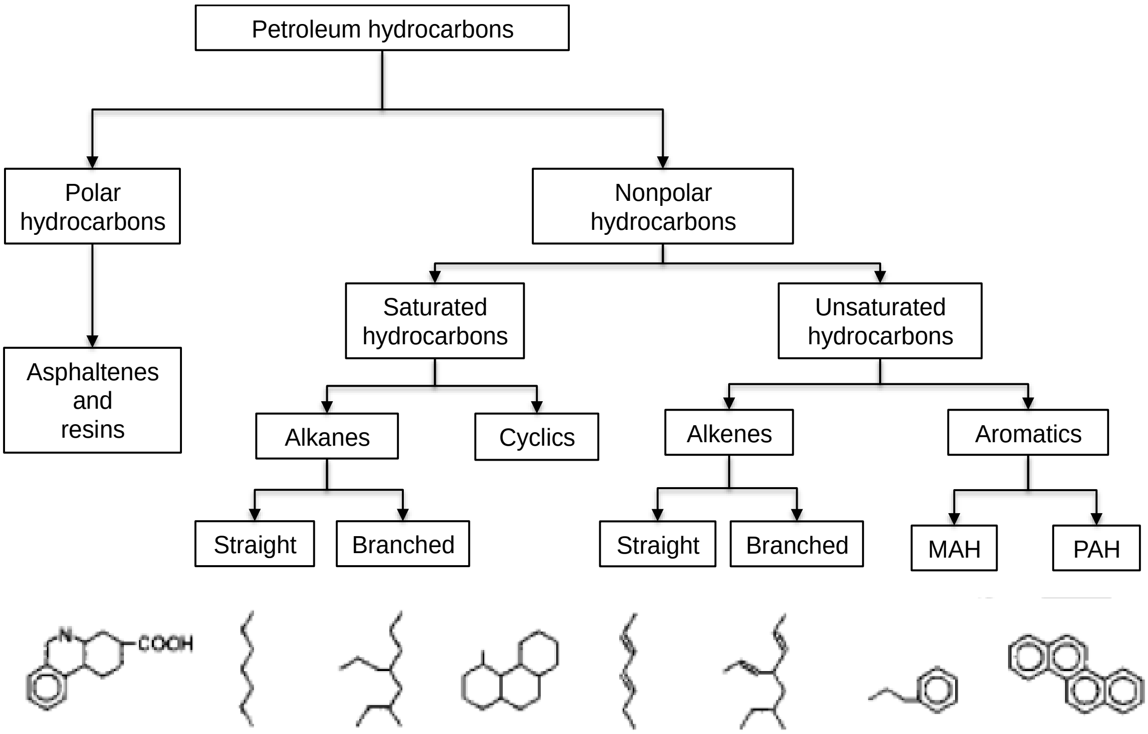
The purpose of this report is (1) to provide information that will facilitate the broader use of various field analytical technologies for the determination of petroleum hydrocarbons (TPH) content in soil; (2) to provide a guidance on the selection of field analytical technologies for site investigation, remediation and verification, and (3) to encourage information exchange between various stakeholders.

The overview of the existing field screening technologies for hydrocarbons determination in soils is based on a targeted literature search of the field analytical techniques currently available, with reference to the scientific basis, reliability, detection limits and precision of the techniques. The limitations and restrictions of the available technologies and any quality assurance measure that should be put in place to verify the field-based data are also discussed.

1.1. DEFINITION OF TOTAL PETROLEUM HYDROCARBONS

Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil and products derived from it. Because there are so many different chemicals in crude oil and in other petroleum products, it is not practical to measure each one separately. Petroleum hydrocarbons can be grouped according to their chemical structure into aliphatic or aromatic hydrocarbons (**Figure 1**), of which saturated aliphatic hydrocarbons link through single bonds as either straight-chains, branched-chains, or non-aromatic rings, e.g. *n*-alkanes and cycloalkanes. Unsaturated compounds bond through double bonds or triple bonds such as *n*-alkenes or alkynes, respectively.

Figure 1: Hydrocarbon compound groups based on their chemical structure (MAH: monoaromatic hydrocarbons; PAH: polycyclic aromatic hydrocarbons) reproduced from Coulon and Wu, 2014.



The aromatic fractions usually comprise two or more aromatic rings. Whereas non-hydrocarbon fractions such as resins (e.g. carbazoles, thiophenes and oxygenated hydrocarbons) and asphaltenes, include other chemical elements in their chemical structure such as nitrogen, sulphur and oxygen.

Based on ISO Standards, TPH is the sum of the measurements using ISO 16703, and the aliphatic and aromatic compounds can be measured based on ISO 22155 or ISO 15009 (ISO, 2009). The various petroleum mixtures are conventionally described by the carbon number range of straight chain *n*-alkanes in the fraction (**Table 2**). Gasoline comprises a mixture of volatile hydrocarbons C_4 to C_{12} with boiling points ranging from 40 to 200 °C, while diesel fuel is predominantly in the C_8-C_{21} range, including aliphatic (approximately 64%), oleofinic (1-2%) and aromatic compounds (35%) (Lominchar et al., 2018). The heavier fractions (> C_{30}) comprise high viscosity, density, boiling points and long residence times in soil (Wang et al., 2019).

Table 2: Petroleum distillation fractions and petroleum products and respective boiling points (US EPA 2000; ISO, 2009).

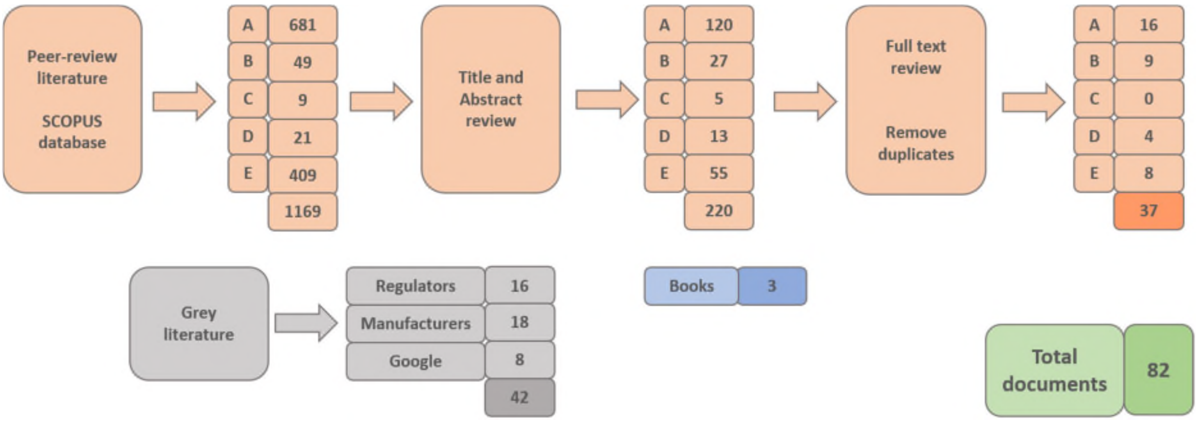
Petroleum fuel mixture	Distillation Fraction	Boiling point (°C)	Compound classes
Gasoline / petrol	C_4 to C_{12}	40 to 215	Gasoline and solvents, including BTEX (benzene, toluene, ethylbenzene and xylene). Mono-aromatics and branched alkanes. Lower concentrations of n-alkanes, alkenes, cyclo-alkanes and naphthalene. Very low concentrations of PAHs.
Kerosene / jet fuel	C_5 to C_{16}	160 to 260	Complex mixtures which may contain up to 260+ aliphatic and aromatic hydrocarbon compounds including toxicants such BTEX, trimethylpentane, methoxyethanol, naphthalene.
Diesel	C_8 to C_{21}	200 to 325	High concentrations of *n*-alkanes. Lower concentrations of branched alkanes, cyclo-alkanes, monoaromatics, naphthalene and PAHs. Very low concentrations of BTEXs.
Fuel oil	C_{12} to $>C_{35}$	350 to 700	High concentrations of *n*-alkanes and cyclo-alkanes. Lower concentrations of naphthalene and PAHs. Very low concentrations of BTEXs.
Motor oils	C_{18} to $>C_{34}$	325 to 600	High concentrations of branched alkanes and cyclo-alkanes. Very low concentrations of BTEXs and PAHs
Crude oil	C_1 to $>C_{35}$	-	High concentrations of *n*-alkanes, branched alkanes and cycloalkanes Lower concentrations of BTEXs, PAH excluding naphthalene. Variable concentrations of sulphur heterocyclics.

When analysing TPH in soil, it is important to keep in mind that hydrocarbon compounds found within soils are derived from many sources and from an analytical perspective, it is difficult to distinguish hydrocarbons originating from petroleum and petroleum-based products from those derived from non-petroleum or non-petroleum-based sources, such as coal, animal or plant origin. Thus, some of the field analytical technologies described in this report do not always differentiate between petroleum-derived material and non-petroleum-derived material from other sources. However, interferences may be minimised using specific clean-up steps.

1.2. DATABASE SEARCH AND TARGETED GREY LITERATURE METHOD

A structured review of the literature was conducted to summarize the current state of the field analytical technologies for TPH determination in soil (**Figure 2**). Amongst the three major abstract and citation databases, Google Scholar, Scopus and the Web of Science, the peer-reviewed literature was sourced from Scopus database since it has a broader coverage than the Web of Science. Further details regarding the screening of the articles are provided in **Appendix 1.1**.

Figure 2: Graphic illustrating selection of sources for this report. Letters A – E refer to terms used in literature search and these are described in the text and Appendices. Numbers are the number of documents assessed, with totals shown in a darker shade.



Overall, a total of 82 documents relevant to the purpose and scope of the work has been identified. While the technologies used for the detection and quantification of TPH in soil are well established and thoroughly discussed in peer-reviewed literature (this resulted in a large number of hits), the testing and performance evaluation of field-based techniques however resulted in fewer hits (17 documents) which have been used to inform the development of Section 2.

2. FIELD ANALYTICAL TECHNOLOGIES FOR THE DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS IN SOIL

2.1. OVERVIEW OF THE ANALYTICAL TECHNIQUES

A wide range of analytical techniques are currently available for the detection and characterisation of petroleum hydrocarbons in soil including chromatographic and spectroscopic techniques, fibre optics, ionization, colorimetry, turbidimetry, immunoassays and bioassays. An overview of the technologies is provided in **Table 3**, and details on the principles of each analytical technique are provided in **Appendix 1.2.**

Analytically, there are four major target lists of hydrocarbons compounds including

- **Volatile organic compounds (VOCs) analysis** which includes a range of selected low molecular weight aliphatic and aromatic hydrocarbons up to EC_{12};
- **BTEX analysis** – a variant on VOC analysis which specifically targets benzene, toluene, ethylbenzene and the three xylene isomers; and
- **Semi-volatile organic compounds (SVOCs) analysis** which includes targets compounds in the range EC_{12} to EC_{40}.
- **PAH analysis** which is a variant of SVOC analysis targeted at polycyclic aromatic hydrocarbons (PAH). This is usually the 16 US Environmental Protection Agency PAHs (USEPA list of priority pollutants specified in the Clean Water Act of 1977, also referred to as 16 USEPA or 16- PAH).

Generally, EC_5 to EC_{12} hydrocarbons are determined and quantified using purge and trap technique or headspace system with gas chromatography and flame ionization, photoionization or mass spectrometry detection while EC_{12} to EC_{40} hydrocarbons are determined and quantified using a particular solvent or a solvent mixture followed by selected detection techniques.

- Among the analytical techniques, GC-based techniques are preferred for petroleum hydrocarbons measurement because they detect a broad range of hydrocarbons, providing both sensitivity and selectivity, and can be used for the determination of the composition (in terms of specific hydrocarbon content) of the hydrocarbons.
- Optical techniques including spectroscopic- and fluorescence-based techniques, on the other hand, do not require any sample extraction with solvents, and provide fast and cost-effective detection of hydrocarbons. The detection is however not selective and do not provide information on the composition, except for ultraviolet fluorescence spectroscopy which is specific to aromatic hydrocarbons.
- Other techniques such as colorimetry allow to determine petroleum hydrocarbons concentration according to the intensity of a coloured solvent solution measured using either a reflectance or absorbance colorimeter, or visually monitored using colorimetric test kits. They do not no information as to the composition (in terms of specific hydrocarbon content) of the extracted hydrocarbons.

- Immunoassay techniques are another alternative characterised by the use of biologically engineered antibodies to bind selectively with a target compound. In general, the immunoassay kits are simple and quick to use, and often used for semi-quantitative screening of petroleum hydrocarbons in soil. They are best suited for the analysis of aromatic compounds (hydrocarbon fraction below EC_7) and aliphatic hydrocarbons ($<EC_{11}$).
- For turbidimetry, the technique is most sensitive to hydrocarbon compounds ranging from C_{12} to C_{30}, including diesel fuel and kerosene, with greatest sensitivity at the high end of the range (US EPA, 2016). The operating principle is based on a methanol-based solvent extraction from hydrocarbons in soil. The concentration of TPH in soil is directly proportional to the amount of petroleum hydrocarbons present in solution.

Each field analytical technique varies in terms of accuracy and precision and as a quick reference, three Data Quality Levels (DQL) can be defined as follows:

Qualitative DQL: provides evidence of the presence or absence of a range of chemical compounds and/or targeted compounds, thus providing indication of the presence of soil contamination. However, when analysing qualitative data, it is not possible to infer about the level of contamination present in soil. Some measurement test kits rely on visual inspection to deliver an immediate qualitative screening.

Semi-quantitative DQL: establishes a relative concentration/ the order of magnitude of the contamination, and this can be useful to assess and define the locations of known types of contamination (e.g. field-based spectroscopy kits).

Quantitative DQL measures accurately a group of contaminants, e.g. BTEX, or its constituents with known reproducibility, accuracy and precision, such as gas chromatography technology. A laboratory grade quantitative analysis uses standard regulatory testing methods for petroleum hydrocarbons analysis in comparison with known concentration standards.

Table 3: Overview of the analytical techniques for the detection of petroleum hydrocarbons in soil.

Technique	Target analytes	Analysis Time (min)	DQL	Skill Level	Advantages	Limitations
Gas chromatography	VOC / BTEX / SVOC/ PAH	5 - 15	Semi-quantitative to Quantitative	High	• Person portable. • Allows separation and identification between aliphatic and aromatic fractions. • Determination of hydrocarbon content	• High degree of expertise required. • Hydrocarbon separation power is limited particularly above the gasoline range, due to the use of shorter GC columns (10-15 m). • Cannot be used for non-volatile compounds or compounds that decompose when vaporised. • Potential for coelution peaks.
Photoionization / Flame ionization detectors (PID/ FID)	VOC / BTEX	10 - 20	Semi-quantitative	Low	• In-situ real-time monitoring. • Fast response.	• Detection is not compound specific. • Cross-reactivity to many volatile hydrocarbons. • FIDs require a source of ultra-pure hydrogen; this requires special handling and shipping. • Adverse environmental conditions: high humidity (e.g., 90%), >1% CH_4, low O_2 (<15%), temperature below 0 C.
Infrared (IR) Spectroscopy	SVOC however, results biased toward > C_{12} because of their greater response to IR	1	Semi-quantitative to quantitative	Medium	• Measurement of multiple chemicals at one time. • Large linear range.	• Detection is not compound specific. • Low sensitivity. • It is not effective for measuring VOCs. • Requires solvent extraction. • High humidity/water interferes to FTIR. • For best detection limits requires cryogenic cooling. • Spectral interpretation requires a skilled user.
Mid-infrared (MIR) Spectroscopy	VOC / SVOC EC_{10} to EC_{40}	3 - 5	Semi-quantitative to quantitative	Medium	• Does not require any sample extraction with solvents. • Fast detection of hydrocarbons. • Excellent accuracy (98%) for hydrocarbon analysis. • Low cost. • Portable.	• Detection is not compound specific. • Sample preparation is required and usually involves removal of debris and homogenisation prior to each measurement. • Sensitive to moisture content greater than 5%. • Requires calibration for each new site. • Cross-validation of calibration samples with a GC system is required.
Visible near infrared (Vis-NIR) Spectroscopy	VOC / SVOC EC_{10} to EC_{40}	3 - 5	Semi-quantitative to quantitative	Medium	• Does not require any sample extraction with solvents. • Fast detection of hydrocarbons. • Reproducible. • Portable.	• Detection is not compound specific. • Potential interferences by soil features such as moisture content, soil type and ambient lights. • Overlapping spectra. • Requires calibration for each new site. • Cross-validation of calibration samples with a GC system is required.

Table 3 Cont'd

Technique	Target analytes	Analysis Time (min)	DQL	Skill Level	Advantages	Limitations
Raman Spectroscopy	SVOC but higher sensitivity towards PAH	< 1 min	Semi-quantitative to quantitative	Medium to High	• Rapid. • Portable. • Long wavelengths limit the interference from fluorescence. • No waste generated.	• Presence of noise limits the detection limit of a particular compound. • Care is needed to avoid laser alteration of samples. • High cost. • High Safety requirements.
Ultraviolet Fluorescence Spectroscopy	SVOC but higher sensitivity towards PAH	5 - 10	Semi-quantitative to quantitative	Low to medium	• Easy to use. • While training is necessary, personnel do not require high skills. • Measures TPH regardless of weathering.	• Specificity to aromatic hydrocarbons. • Response factor must be developed to measure aliphatic hydrocarbons, and this cannot be done in the field but in the lab. • Fluorescence response is sensitive to soil matrix.
Colorimetry	Aromatic SVOC	10 - 20	Qualitative to semi-quantitative	Low to medium	• This method is not dependent on analyte volatility, thus particularly useful for detection of older spills.	• The extraction efficiency in clay soils is problematic. • Colours may be difficult to distinguish through visual inspection, particularly TPH at low concentrations. • Potential for overestimation of concentrations - should be determined within 30 minutes of colour formation.
Detector Tubes	VOC / BTEX	5 - 15	Qualitative to semi-quantitative	Low	• Relatively easy to use. • Provide readings in the parts-per-million (ppm) range, although some can detect as low as ppb.	• High degree of cross-reactivity. • Tubes specific to individual compounds (or group of compounds)
Immunoassays	BTEX / SVOC / PAH	30 - 60	Qualitative to semi-quantitative	Medium	• Used to assess whether samples are above or below an action level - particularly useful to assist with remediation strategies. • Low cost.	• Designed to test for a range of hydrocarbons or specific analytes only. • Potentials for false positives results due to cross-reactivity to many hydrocarbon constituents. • Heavy petroleum hydrocarbon fractions are not detected. • The operating working temperature should be maintained at 4 °C - 32 °C. • The test kits should not be used beyond the expiry date.
Emulsion Turbidimetry	SVOC (C_{12} - C_{30} including diesel fuel and kerosene)	15 - 20	Qualitative to semi-quantitative	Low to medium	• Measurement of total petroleum hydrocarbon (TPH) content in soil.	• Light-weight petroleum hydrocarbons (e.g., gasoline) are not detected. • Potential for false positive interferences from organic-rich soils. • High soil moisture content may cause negative interferences. • Filtration efficiency may be problematic specially with clay soils. • Temperature range of operation is 4 to 45˚C.

Table 3 Cont'd

Technique	Target analytes	Analysis Time (min)	DQL	Skill Level	Advantages	Limitations
Fibre Optic Chemical Sensors (FOCS)	VOC (^{3} C_6) and SVOCs	3 - 10	Qualitative to semi-quantitative	Low	• In-situ real-time monitoring. • Small and flexible fibres enabling access to difficult locations.	• Detection is not compound specific. • Sensors response is temperature compensated. • Readings provide a relative value, a response factor (empirically determined by the manufacturer) must be used to estimate contaminant levels.

2.2. PORTABLE INSTRUMENTS AND FIELD TEST KITS

A large variety of field instruments and kits exist for the determination of petroleum hydrocarbons in soil ranging from qualitative to quantitative measurements. There are also a wide range of applications for field technologies, for example simple checks in order to identify if a contaminant is present or absent, detailed mapping of contamination across a site and monitoring of contaminant plume dispersal. However, selecting the most appropriate field screening technique for petroleum hydrocarbons analysis in soil can be difficult and will depend on the intended application or purpose of the measurement, such as the need for qualitative, semi-quantitative or quantitative data. To assist with this task, an overview of the portable instruments and field test kits considered in this report is provided in **Table 4**. For each of them, the type of analytes, associated method sensitivity, detection limit, linearity and accuracy are reported. A brief description for each of them and the points to be considered for their selection is provided in the following sub-sections. Further details on the description and operating procedures for each instrument or kit can be found in the **Appendix 1.3**.

Table 4: Detection limit, hydrocarbons group, sensitivity, operating range, linearity and accuracy of the portable instruments and field test kits.

Instrument/ field test kit	Technology	DQL	Analytes detected	DL[a]	Sensitivity [b] or Operating Range	Linearity [c]	Accuracy [d]
HAPSITE® INFICON® Inc	Gas chromatography-mass spectrometry	Semi-quantitative to Quantitative	VOC / BTEX / SVOC/ PAH	0.001 mg/kg (1 ppb)	1-10 ppb (full scan); 1-10 ppt (SIM) for individual hydrocarbons compounds	10^5-10^6 41 – 300 amu using full scan 1 – 300 amu using SIM)	± 8%
Portable FLIR Griffin™ G510 GC-MS	Gas chromatography-mass spectrometry	Semi-quantitative to Quantitative	VOC / BTEX / SVOC/ PAH	1 ppb to 1 ppt	1-10 ppm (full scan); 1-10 ppt (SIM) for individual hydrocarbons compounds	10^5-10^6 15-515 m/z; 0.7 amu @ FWHM	± 8%
Torion T-9 Portable GC MS Perkin Elmer	Gas chromatography-mass spectrometry	Semi-quantitative to Quantitative	VOC / BTEX / SVOC/ PAH	ppb to ppt	1-10 ppb (full scan); 1-10 ppt (SIM) for individual hydrocarbons compounds	10^5-10^6 41-500 m/z/ better than unit mass resolution from 41 - 300 amu and nominal mass resolution up to 500 amu.	± 8%
Environmental and BTEX GC Systems SRI INSTRUMENTS	Gas chromatography	Semi-quantitative to Quantitative	VOC / BTEX	PID - ppb range/ Purge & trap - down to ppt range	0.1 – 10 ng/kg	10^5-10^6 mg/kg	± 10%
FROG-5000™ Portable GC	Gas chromatography	Semi-quantitative to Quantitative	VOC / BTEX	PID - ppb range	1-10 ppb	10^5-10^6 mg/kg	± 10%
Handheld Flame ionisation detector (FID) Micro FID II	Flame ionization detector	Semi-quantitative	VOC / BTEX	0.1 mg/kg	0.1 – 50,000 mg/kg	105-106 mg/kg	± 5%
PID MiniRAE (10.6 eV lamp)	Photoionization detector	Semi-quantitative	VOC / BTEX	0.1 mg/kg	0.1 – 15,000 mg/kg	105-106 mg/kg	10 to 2000 ppm: ±3% at calibration point
Infracal® TOG/TPH Analyser Model	Infrared (IR) spectroscopy	Semi-quantitative to Quantitative	SVOC	1 mg/kg	1.0 to 2,000 mg/kg	Dependant on sample concentration ratio	± 1%
ASD FieldSpec 4 Hi-Res Spectroradiometer	Vis-NIR spectroscopy	Semi-quantitative to Quantitative	VOC / SVOC (optimal response EC_{10}-EC_{40} banding)	1 mg/kg	0.1 – 50,000 mg/kg	0.5 to 50,000 mg/kg	± 0.5 nm

Table 4 Cont'd

Instrument/ field test kit	Technology	DQL	Analytes detected	DL[a]	Sensitivity [b] or Operating Range	Linearity [c]	Accuracy [d]
RemScan®	MIR FTIR spectroscopy	Semi-quantitative to Quantitative	VOC / SVOC (EC_{10}-EC_{40} banding)	68 mg/kg	0.1 to 100,000 mg/kg	100-100,000 mg/kg	± 1-3% of reading
4300 Agilent Handheld FTIR	MIR-FTIR spectroscopy	Semi-quantitative to Quantitative	VOC / SVOC (EC_{10}-EC_{40} banding)	1 mg/kg	0.1 - 50,000 mg/kg	0.5 to 50,000 mg/kg	RSME = 1592 mg/kg and $R^2 = 0.89$
QualitySpec Trek	Vis-NIR spectroscopy	Semi-quantitative to Quantitative	VOC / SVOC (EC_{10}-EC_{40} banding)	1 mg/kg	0 - 50,000 mg/kg.	0.5 to 50,000 mg/kg	± 5%
Horiba OCMA-350 Oil Content Analyser	Infrared (IR) spectroscopy	Quantitative	aromatic SVOC	1 mg/kg	0 - 1,000 mg/kg	1 - 1000 mg/kg	± 5%
SiteLab Analytical Test Kit UVF-3100A	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	VOC / aromatic SVOC	3.4 mg/kg	0 to 2,000 ppm as TPH	Compound specific, ppm	± 10% of reading
Rapid Optical Screening Tool (ROST®)	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Aromatic SVOC	10 mg/kg	Site dependent	Up to 10,000 mg/kg	89% agreement with discrete soil sample analytical results
SCAPS LIF sensor	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Aromatic SVOC	10 mg/kg	Site dependent	Up to 10,000 mg/kg	90% agreement with discrete soil sample analytical results
TarGOST®	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Aromatic SVOC	100 mg/kg	Site dependent	Up to 10,000 mg/kg	98% agreement with discrete soil sample analytical results
UV LED	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Aromatic SVOC	100 mg/kg	Site dependent	Up to 10,000 mg/kg	98% agreement with discrete soil sample analytical results
UVOST®	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Aromatic SVOC	10 mg/kg	Site dependent	200-10,000 mg/kg	98% agreement with discrete soil sample analytical results
DyeLIF™	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	Chlorinated aliphatic SVOC	10 mg/kg	Site dependent	Up to 10,000 mg/kg	98% agreement with positive DNAPL detections in samples where DNAPL pore saturations were >0.7% (based on quantitative soil analyses)

Table 4 Cont'd

Instrument/ field test kit	Technology	DQL	Analytes detected	DL[a]	Sensitivity [b] or Operating Range	Linearity [c]	Accuracy [d]
Hanby TPH Soil kit	Colorimetry	Qualitative and semi-quantitative	BTEX / SVOC / PAH	1 mg/kg	N.A.	1.0 - 1,000 mg/kg	± 5%
Dräger Detector Tubes	Colorimetry	Qualitative to semi-quantitative	VOC / BTEX	compound specific	compound specific	2 -1,400 mg/kg	compound specific
RaPID® BTEX/TPH Assay	Immunoassay	Qualitative to semi-quantitative	VOC / BTEX	0.9 mg/kg total BTEX	0.9 ppm to 30 ppm for BTEX TPH range varies based on fuel source.	Not compound specific, ppb to ppm range	N.A.
PetroFLAG® test kit	Emulsion turbidimetry	Qualitative to semi-quantitative	VOC / BTEX / SVOC / PAH	15 mg/kg	BTEX 16 -140 mg/kg; Petrol 80 - 600 mg/kg; PAH 8 - 60 mg/kg TPH 15-2,000 mg/kg	Not compound specific, 10 - 2,000 mg/kg	± 10%

Key: N.A. not applicable.[a] Detection limit (DL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results. [b] Sensitivity describes the smallest absolute amount of change that can be detected by a measurement which is often referred to as the limit of detection (LoD) [c] Linearity of an analytical method can be explained as its capability to show "results that are directly proportional to the concentration of the analyte in the sample". Linearity is often measured within a given range. [d] Accuracy describes the amount of uncertainty that exists in a measurement with respect to the relevant absolute standard

2.2.1. Field gas chromatography-mass spectrometry systems

With field gas chromatography-mass spectrometry (GC-MS) systems, a broad spectrum of TPH can be analysed. Field portable or transportable gas chromatographic analysis can be of equal quality as fixed laboratory data when proper quality control is performed (CLUN-IN, 2020a). Instrument operation requires a higher degree of expertise than most other field instrumentation. Common limitations to field GC include potential for coelution of analytes in single column systems, sample carryover and equipment contamination. A comparative evaluation of portable field GC-MS systems is provided in **Table 5**.

Table 5: Comparative evaluation of advantages and limitations between field portable gas chromatograph mass spectrometers.

Product	Advantages	Limitations
 HAPSITE portable GC-MS system (Inficon)	• Probe for sampling vapours for rapid survey analysis. • Fully hot swappable carrier gas cylinders of nitrogen. • Fully charged battery provides 2 to 3 hours of operation time • High accuracy and sensitivity • Identify specific analytes and actual concentrations reported • Reduce shipping and analytical costs in remote locations.	• AMU and GC column temperature range limit the range of compounds that can be identified. • Portable containers of inert gas can be costly. • Multicomponent (and therefore multipeak) compound interferences with single peak compounds, e.g. BTEX or Alkanes and PAHs. • Proprietary NiMH battery; long recharge time • Operating temperature range not sufficient for winter conditions in some regions.
 Portable GC-MS FLIR Griffin™ G510 (FLIR Systems)	• AMU and GC column temperature ranges allow a wide range of chemical compounds to be identified. • Integrated injector allowing injection of organic liquids. • Equipped with an air-sampling probe for vapour analysis. • Sample port readily accepts a range of sample types. • Fully hot swappable, non-proprietary Li-ion batteries • Operating time is approximately 2 hours in survey mode and 1 hour in full GC/MS mode	• Does not indicate carrier gas level • Portable containers of inert gas (Helium) can be costly. • Operating temperature range not sufficient for winter conditions in some regions.
 Torion T-9 Portable GC-MS (Perkin Elmer).	• AMU and GC column temperature ranges permit a wide range of chemical compounds to be identified. • Organic liquid samples can also be directly injected for analysis. • Low power consumption. • Non-proprietary Li-ion battery.	• No vapour sampling probe and cannot perform survey analysis • Portable containers of inert gas (Helium) can be costly. • Operating temperature range not sufficient for winter conditions in some regions.

Table 5 Cont'd

Product	Advantages	Limitations
 Environmental GC System (Instruments SRI).	- Methanol interference is not detected by PID. - Detectors in series: peak overlap in FID signal is detected in the PID chromatogram. - Substantial lower cost once compared to a field GC-MS.	- The PID detector is prone to cross-sensitivity to many volatile hydrocarbons. - The use of Hydrogen for combustion on FID. - FID does not detect compounds selectively. - Many aliphatic compounds cannot be detected with this equipment due to the use of a PID detector.
 Frog-5000 portable GC (Defiant Technologies).	- Detection of VOC analytes with ionization below 10.6eV - Does not need external carrier gas. - Lightweight - weighs less than 2.2 kg - Quantitative results display on screen.	- Is not recommended for analysis of diesel. - Detection of VOC analytes with ionization below 10.6 eV only. - Potential for cross-reactivity to many volatile hydrocarbons. - Operating temperature range not sufficient for winter conditions in some regions

Points to consider in the choice of a field GC:

Field portable, or transportable	A portable GC should be self-contained, need no exterior power source, weigh less than 10 kg, be easily portable by a single person, and be capable of operating for a day's field work (8 hours) without consumable supplies being replenished. Transportable GC systems are instead packed into a crate for shipping and transported by truck or van. These instruments are not hand portable, and generally require operation from the back of a van.
Durability	Is the GC capable of handling adverse conditions? Can it operate in conditions of high humidity, high and low ambient temperatures? Will the operator be able to use the GC when wearing mandated personal protective equipment such as gloves? Is the instrument rugged?
Ease of operation	Are the instrument's controls easy to use when the operator's hands are cold? Are the panels that display results or operating parameters, easy to read, even in poor lighting conditions?
Applicability	Can the instrument manufacturer customize the GC to your requirements? Does the manufacturer provide "hands-on" training on the system, or do they provide instructional videos?
Detection limits	Can the instrument achieve the detection limits required?
Dynamic range	Does the GC have a wide dynamic range, reducing the need for sample dilutions?
Sample Turn-around	What kind of sample throughput can be expected? Is the introduction of the sample into the GC straightforward?
Sample delivery options	Does the instrument support a variety of sampling techniques, such as loop and syringe injection, sampling by probe, solid phase microextraction (SPME)?

2.2.2. PID and FID detectors

Photoionization detector (PID) or a flame ionization detector (FID) are both sensitive to low-range gases and vapours, mainly volatile organic compounds (VOCs). PID and FID will not give the same readings in an identical gas stream. PID is more sensitive to functional groups, whereas FIDs respond to the length of the carbon chain. **Table 6** summarises the advantages and limitations between detectors.

Table 6: Comparative evaluation of advantages and limitations between FID and PID detectors.

Product	Advantages	Limitations
 **MicroFID II Portable Flame Ionization Detector (Environmental Monitoring).**	• Sensitive response to compounds that are ionized in a hydrogen-air flame (organic compounds) but not to air, water, or light gases. • Response factors between aliphatic and aromatic hydrocarbons are essentially the same, making it equally adequate to analyses either group of organic compounds. • Allows separation and identification between aliphatic and aromatic fractions. • FID more sensitive to aliphatic compounds than PID. • Less sensitive to humidity than PIDs • Low skill/ training levels required for use.	• FID does not detect compounds selectively. • Cross-reactivity to many volatile hydrocarbons. • FID provide semi-quantitative results only which is typically referenced to isobutylene.
 **(A) MiniRAE photoionization detector (PID) and (B) RKI Eagle 2 PID Instrument (Ribble Enviro Ltd)**	• PID can detect VOCs (aromatic and chlorinated) and petroleum constituents including benzene, toluene, ethylbenzene and xylene (BTEX). • High sensitivity and fast response time. • Relatively low cost. • Low skill/ training levels required for use. • Methane can be eliminated, by lamp selection, reducing biased high readings. • Data logging capabilities	• Many aliphatic compounds cannot be detected with PID. • Cross-reactivity to many volatile hydrocarbons. • The instrument will only detect constituents with an ionization potential less than the lamp energy. • Instrument and measurements can be affected by soil type, moisture, constituent chemistry, sample temperature and hold times. • PID provide semi-quantitative results only which is typically referenced to isobutylene.

Points to consider in the choice of FID or PID: The selection of the most appropriate detector, either FID or PID, depends on the target compound under study. FIDs are more sensitive to aliphatic (or chained) hydrocarbons than PID because these compounds burn more efficiently than aromatic (or ringed) hydrocarbons (US EPA, 2016), while PID can only detect VOCs (aromatic and chlorinated) and petroleum constituents including benzene, toluene, ethylbenzene and xylene (BTEX) with an ionization potential lower than the lamp energy.

2.2.3. Field spectrometric systems

The basic principle of operation relies in the absorption of energy in the infrared (IR), near-infrared (NIR) and mid-infrared (MIR) region of the electromagnetic spectrum. A comparative evaluation of advantages and limitations of field and portable spectrometric systems is summarised in **Table 7**.

Table 7: Comparative evaluation of advantages and limitations between field spectrometers.

Product	Advantages	Limitations
 InfraCal TOG/TPH analyser, model HATR-T2 (Wilks Enterprise)  InfraCal TOG/TPH analyser model CVH (Wilks Enterprise)  InfraCal 2 (latest version with added features; Spectro Scientific)	• Measurement of multiple chemicals at one time. • Large linear range. • The device can be operated by one person with basic wet chemistry skills. • Quantitative results. • CVH and Infracal 2 measure all hydrocarbons	• Soil moisture content can have a statistically significant impact on diesel sample results but not on weathered gasoline sample results. • Requires solvent extraction. • Soil type is an important consideration because the extraction efficiency is much higher in sands than in clays. • HATR-T2 Measures hydrocarbons with a boiling point higher than the solvent—volatile hydrocarbons will be evaporated along with the solvent.
 ASD FieldSpec 4 Hi-Res Spectroradiometer (Panalytical ASD Malvern)	• Useful for detecting and identifying compounds with narrow spectral features in the longer wavelengths. • Full-range detection capacity (350 – 2500 nm) provides uniform VIS/NIR/SWIR data collection across the entire spectrum. • Fast integration speed allows for high-quality measurements in a limited amount of time.	• Without LCD display. • Without GPS • Sample preparation is required and usually involves air-drying samples, removal of debris and homogenisation. prior to each measurement • Sensitive to moisture content greater than 5%. • Cross-validation of calibration samples with a GC system is required.

Table 7 Cont'd

Product	Advantages	Limitations
 RemScan® handheld mid-infrared instrument (Ziltek)	• Does not require any sample extraction with solvents. • Fast detection of hydrocarbons (15-30s) • Accuracy 98% for hydrocarbon analysis (C_{10} - C_{40}). • The signal is displayed in concentration (mg/kg) on the PDA or Tablet. • Easy to standardise in the field – 1-minute background cap, 1-minute reference cap (both are inert materials so no need to carry calibration gases or hazardous chemicals). • Requires low level of skill. • For high moisture applications, a portable drying unit can be used to dry up to 35 soil samples in 30-60 minutes.	• Detection is not compound specific. • Sample preparation is required and usually involves air-drying samples, removal of debris and homogenisation prior to each measurement. • Sensitive to moisture content greater than 5%. • Requires calibration for each new site. • Cross-validation of calibration samples with a GC system is required.
 Agilent 4300 Handheld FTIR Spectrometer (Agilent)	• Does not require any sample extraction with solvents. • Enhanced models have accuracy comparable to the RemScan® Spectrometer. • Intuitive touch-screen user interface. • Fast sample measurement (15-30s)	• Detection is not compound specific. • Sensitive to moisture content. • Sample preparation is required and usually involves air-drying samples, removal of debris and homogenisation prior to each measurement. • Data is displayed as IR spectral response and not concentration.
 QualitySpec Trek spectrometer (Panalytical ASD Malvern)	• Battery operated. • Does not require any sample extraction with solvents • on-board GPS, voice audio recorder for expanded sample descriptions, • Internal white reference for hands-free optimization and calibration	• Detection is not compound specific. • Requires calibration for each new site • Sample preparation is required and usually involves air-drying samples, removal of debris and homogenisation prior to each measurement. • Sensitive to moisture content
 **Horiba OCMA-350 Oil Content Analyser (Horiba).**	• Targets mid- to high range hydrocarbons (C_{10}-C_{36}). • Solvent extract does not generate hazardous waste. • Measured concentration is displayed on the LCD screen.	• Although portable is not a handheld device (weight, approx. 5 kg). • Soil analysis subject to extraction. • Requires field lab—not a rugged portable instrument. • Requires specialised training and wet chemistry skills.

Points to consider in the selection of a field spectrometer:

Field portable, or transportable	Is the device portable and lightweight, and is the equipment rugged?
Wavelength range	The spectroscopic characteristics of the substance being monitored determine the wavelength range needed. Most organics can be identified in near-IR and IR.
Spectral resolution	Once the desired wavelength range for a spectrometer is determined, spectral resolution needs to be considered, which determines the ability to separate adjacent spectral features.
Wavelength accuracy	The wavelength accuracy is the accuracy of the wavelength values attributed to an output spectrum and is influenced by wavelength drift caused by temperature changes.
Resolution	Resolution depends on detector type and involves issues such as the smallest detectable changes and the lowest absolute amount of detectable energy, dynamic range, signal stability, and linearity.
Durability	Is the device capable of handling adverse conditions? Can it operate in conditions of high humidity, high and low ambient temperatures?
Ease of operation	Are the instrument's controls easy to use when the operator's hands are cold? Are the panels that display results or operating parameters, easy to read, even in poor lighting conditions?

2.2.4. Field fluorescence systems

Petroleum hydrocarbons can be detected with fluorescence techniques due to the presence of highly fluorescent components like polycyclic aromatic hydrocarbons (PAH). This technology is suitable for measuring the aromatic hydrocarbon portion of TPH independent of their carbon range. Aliphatic hydrocarbons do not fluoresce; thus, these cannot be detected by this technology. A comparative evaluation of advantages and limitations of portable and field fluorescence systems is provided in **Table 8**.

Table 8: Comparative evaluation of advantages and limitations between field fluorescence systems.

Product	Advantages	Limitations
 Sitelab - Model UVF-3100A and UVF-3100D Use for GRO, EDRO, PAH and TPH fingerprinting (SiteLAB)	• Quantitative measure of TPH; can also measure both GRO and EDRO compounds of all fuel types regardless of weathering. • Easy to operate, low skill required and fast • The UVF-3100A uses reusable, certified standards for calibration.	• Specificity towards aromatic hydrocarbons. • Response factor must be developed to measure aliphatic hydrocarbons, and this cannot be done in the field but in the lab. • Fluorescence response is sensitive to soil matrix. • Soil analysis subject to methanol extraction.

Table 8 Cont'd

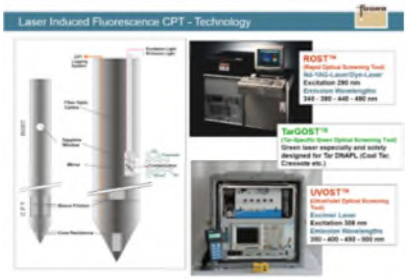
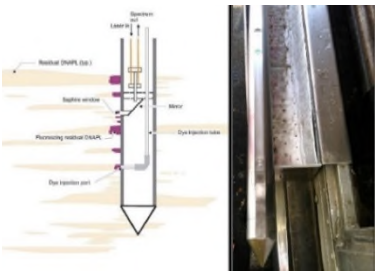
Product	Advantages	Limitations
 Rapid Optical Screening Tool (ROST®) System Overview of LIF CPT technology (Fugro)	- No sample preparation is required. - Ability to collect measurements up to 45 m below the soil. - Able to distinguish hydrocarbon-contaminated areas from uncontaminated areas. - Fluorescence of all aromatic hydrocarbons with at least two conjugated aromatic rings (e.g. naphthalene, phenanthrene but excluding monoaromatics like benzene and compounds where rings are not conjugated (e.g. biphenyl)). - Data can be uploaded into 3-D visualization software.	- Aliphatic hydrocarbons and single-ring aromatics are not detected. - Fluorescence response is sensitive to soil matrix, soil grain size, mineralogy, moisture content and surface area. - Potential spectral interferences to any compounds that fluoresce at UV wavelengths such as humic and fluvic acids. - The CPT support platform used to deploy the ROST LIF is typically a 20-tonne truck. The dimensions of the truck require a minimum access width of 3 m and a height clearance of 4.5 m. Some sites might not be accessible to a vehicle of this size. - The system provides relative data rather than quantitative data. - The operation of the ROST™/CPT requires considerable experience.
 Site Characterization and Analysis Penetrometer System (SCAPS) LIF Sensor and Support System (Fugro)	- No sample preparation is required. - Detection of three or more aromatic rings predominantly. - Able to distinguish hydrocarbon-contaminated areas from uncontaminated areas. - Data can be uploaded into 3-D visualization software.	- Aliphatic hydrocarbons, single-ring aromatics and most two-ring petroleum hydrocarbons are not detected. - Limited to areas where a 20-ton truck can gain access. - The system provides relative data rather than quantitative data. - The operation of the SCAPS requires considerable experience.
 Tar-Specific Green Optical Screening Tool (TarGOST®) (Fugro)	- When mounted on a direct push (DP) platform (non-CPT) can access tight areas and operate inside buildings. - No sample preparation is required. - The system can be used with a variety of direct push equipment.	- The system does not detect light fuels and oils or chlorinated aliphatic hydrocarbons. - The system provides relative data rather than quantitative data. - The operation of the TarGOST requires considerable experience.

Table 8 Cont'd

Product	Advantages	Limitations
 Ultraviolet Light Emitting Diode (UV LED) (Vertek probe system)	• When mounted on a direct push (DP) platform (non-CPT) can access tight areas and operate inside buildings. • No sample preparation is required. • The system can be used with a variety of direct push equipment.	• The system does not readily identify coal tars, creosote, or bunker oil, nor does it detect chlorinated aliphatic hydrocarbons. • Data are not compatible with 3-D visualization software. • The system provides relative data rather than quantitative data. • The operation of the UV LED requires considerable experience.
 UltraViolet Optical Screening Tool (UVOST®) (Top) UVOST® detection system; (bottom) UVOST® mates with direct-push platforms such as Geoprobe and CPT **(**Dakota Technologies**)**	• When mounted on a direct push (DP) platform (non-CPT) can access tight areas and operate inside buildings. • No sample preparation is required. • The system can be used with a variety of direct push equipment. • Data can be uploaded into 3-D visualization software.	• Does not readily identify coal tars, creosote, or bunker oil, nor does it detect monoaromatics or chlorinated aliphatic hydrocarbons. • Provides relative data rather than quantitative data. • Requires considerable experience.
 Dye-Enhanced Laser Induced Fluorescence System (DyeLIF™) (Dakota Technologies) (Left) dye-LIF probe schematic and (right) field photo (Einarson et al., 2014).	• The system identifies chlorinated aliphatic hydrocarbons. • When mounted on a direct push (DP) platform (non-CPT) can access tight areas and operate inside buildings. • No sample preparation is required. • The system can be used with a variety of direct push equipment. • Data are compatible with 3-D visualization software.	• The system provides relative data rather than quantitative data. • The operation of the system requires considerable experience.

Points to consider in the selection of a field fluorescence system:

Field portable, or transportable	Is the device portable?
Abandonment	Can the sample holes be grouted as the push rod is pulled from the hole? Or use a CPT as the push rod is pulled from the hole.
Accessibility	When mounted on a direct push (DP) platform (non-CPT) can it access tight areas and operate inside buildings?
Driving platform	Can the system be used with a variety of direct push equipment or CPT only?
Depth	The depth of perforation of the subsurface.
Spatial resolution	The vertical spatial resolution of instrumentation.

2.2.5. Colorimetric field test kits

Colorimetric test kits provide qualitative or semi-quantitative screening of aromatic hydrocarbons in soil and water. The test kits are selective to aromatic hydrocarbons and the method is not dependent on analyte volatility, thus particularly useful for detection of older spills. The amount of equipment included with each test kit varies widely depending on the type and manufacturer of the kit. Some kits come with colour wheels or colour charts to be used for semi-quantitative analysis. Electronic analysers that detect and analyse the colour change electronically can also be ordered with many kits. The complexity of the kit will depend on the type of test, the sample medium, and the level of data quality required. The only equipment necessary to use indicator tubes are the tubes and a hand pump. Overview of the two main kits commercially available is summarised in **Table 9**.

Table 9: Colorimetric field test kits, advantages and limitations.

Product	Advantages	Limitations
 Hanby TPH Soil kit (Hanby Environmental)	• Ease of use. • Provides semi-quantitative data in the field for TPH. • The test kit does not require batteries or a power source. • This method is not dependent on analyte volatility, thus particularly useful for detection of older spills (weathered hydrocarbons and heavier fuel oils).	• Inaccurate comparison of colour if the sample is dark in colour. • Interpretation of results may be inaccurate because of interference from other petroleum fractions. • Underestimation of concentration for highly refined petroleum fuels (those that are lacking in aromatic compounds). • The kit is not able of distinguishing different hydrocarbon fractions. • Unsuitable for ambient temperatures less than 4°C.

Table 9 Cont'd

Product	Advantages	Limitations
 Dräger Detector Tubes and Accuro pump (Dräger)	• No electronic instrumentation required. • No calibration of detector tubes is required. All materials are provided pre-charged and ready for use • After initial pump purchase, relatively low sample costs • Good repeatability of measurements with comparable matrix and holds times. • Low skill required for use.	• The reading of the tube must be done immediately following the measurement. • Cross-sensitivity with compounds of similar chemical behaviour (i.e. benzene and ethyl benzene) - potential for false positives. • Tubes are compound-specific, requiring one tube for each analyte. • The minimum temperature 0°C and the maximum temperature typically ranges from 30 to 40°C.

Points to consider in the selection of a colorimetric test kit:

Target analytes	The selection of target analytes that the kit is able to detect, e.g. volatiles only, aromatic hydrocarbons etc.
Linear range	The linear range of analysis
Detection limit	Detection limit of the test kit.
Interferences	Several factors can interfere with the detection and quantification of elements in a sample. Some interferences, such as cross-reactivity, are inherent in the analytical method. Other interferences may be caused by outside factors, such as the sample matrix. (e.g. extraction efficiency is matrix dependent).
Data quality	Semi-quantitative or qualitative only.
Application	Soil, water or both?

2.2.6. Immunoassay field kits

In general, the immunoassay test kits are simple and quick to use, and these are often used for semi-quantitative screening of TPH in soil. They are best suited for the analysis of aromatic compounds (hydrocarbon fraction below C_7) and aliphatic hydrocarbons ($<C_{11}$). While several test kits were originally available, only one kit has been identified being commercially available at the time of this report (**Table 10**).

Table 10: Field test kits based on immunoassays, advantages and limitations.

Product	Advantages	Limitations
 RaPID® BTEX/TPH Assay (Modernwater).	- Rapid field-testing of TPH in soil. - Three kit calibrator levels, in units comparable to results from GC method 8015 (TPH). - Soil extraction time typically two minutes per sample plus assay run time of approximately 60 minutes.	- Shelf life is typically one year from date of manufacture. - Reagents must be stored between 4 to 8 °C when not in use. - Store at ambient temperature 18 to 27 °C is acceptable for day of use. - Kits must be brought to 18 to 27 °C before use. - It is unable to differentiate between BTEX and related compounds. - Colour solution cannot be exposed to direct sunlight. - Training recommended. - Requires site specific calibration against laboratory analysis.

Points to consider in the selection of an immunoassay test kit:

Target analytes	Immunoassay kits are available for a wide variety of organic contaminants, including gasoline; diesel fuel; jet fuels; benzene, toluene, ethylbenzene, and xylenes (BTEX); polynuclear aromatic hydrocarbons (PAH).
Interferences	Several factors can interfere with the detection and quantification of elements in a sample. Some interferences, such as cross-reactivity, are inherent in the analytical method. Other interferences may be caused by outside factors, such as the sample matrix.
Detection limit	Although the detection limits vary depending on the test kit manufacturer, target analytes, sample matrix, and interferences, kits are available that can achieve parts per million (ppm), parts per billion (ppb), and even parts per trillion (ppt) detection limits in water samples. Detection limits are higher for soils because extraction is necessary.
Data quality	Semi-quantitative or quantitative.
Precision and accuracy	Precision and accuracy are measures applied to quantitative immunoassay data.

2.2.7. Turbidimetric field test kits

The operating principle is based on a methanol-based solvent extraction from hydrocarbons in soil. The concentration of TPH in soil is directly proportional to the amount of petroleum hydrocarbons present in solution. Field kit currently available is summarised in **Table 11**.

Table 11: Field test kits based on turbidimetry, advantages and limitations.

Product	Advantages	Limitations
PetroFLAG® Analyser System for TPH in soil (DEXSIL) 	• Responds to a broad range of petroleum products regardless of their composition and extent of weathering. • Provides direct measurement of recoverable hydrocarbon concentrations • Easy to operate.	• Light-weight petroleum hydrocarbons (e.g., gasoline) are not detected; • Naturally occurring hydrocarbons (organic-rich soils) may limit the effectiveness of the extraction or cause false positive interferences; • Limited portability once setup • High soil moisture content may cause negative interferences; • Filtration efficiency may be problematic specially with clay soils • The temperature range of operation is 4 to 45 C (US EPA, 2016).

Points to consider in the selection of a turbidimetric test kit:

Target analytes	Turbidimetric test kits cover the C_{12}-C_{40} hydrocarbon range and do not detect the gasoline range.
Interferences	Several factors can interfere with the detection and quantification of elements in a sample. Some interferences, such as cross-reactivity, are inherent in the analytical method. Other interferences may be caused by outside factors, such as the sample matrix, e.g. potential for false positive interferences from organic-rich soils; high soil moisture content may cause negative interferences.
Detection limit	Although the detection limits vary depending on the test kit manufacturer, target analytes, sample matrix, and interferences, kits are available that can achieve parts per million (ppm).

2.3. CALIBRATION AND QUALITY CONTROL REQUIREMENTS

Ensuring that the data generated by the various kits and field technologies is of a known quality is vital to ensuring the usefulness of the data. Several kits require that calibration standards are analysed before analysis begins (**Table 12**). When several standards of known concentration are analysed, the relative response of the test kit at each concentration can be estimated. In that way, the concentrations in the samples that are within the range can be determined accurately. Calibration requirements and quality control (QC) measures take several forms. They can be performed in the field, during sample analysis, or after sample data have been collected. The type and extent of calibrations and QC required will also vary according to the test to be performed and the purpose of the data such as first stage investigation (screening) or second stage investigation (detailed quantitative assessment). Indeed, a much higher level of QC will be necessary to produce defensible data that will be used alone to support specific decisions than to produce screening data that will not be used alone to support decision-making. Examples of steps required for QC for field analytical kits or devices can be found in “Guidance Manual for the Preparation of Demonstration and Quality Assurance Project Plans for the Verification of Field Characterization and Monitoring Technologies” (EPA/540/R-10/001; US EPA, 2010) and the “Performance Standard for Laboratories Undertaking Chemical Testing of Soil” (Environment Agency, 2018, version 5).

Common QC requirements are briefly outlined in general terms below.

- **Method blanks** are "clean" samples of the same matrix as the field samples to be analysed that are taken through all the same sample preparation and analysis steps. The method blanks are used to monitor for (i) contaminants inherent in any of the disposable supplies or reagents; (ii) cross contamination; and (iii) for contamination caused by any other sources, such as poor decontamination procedures for reusable items. Typically, one method blank should be analysed for every 20 regular samples. The sample should not contain any target analytes at concentrations above the test kit’s detection limit. If such concentrations are above the detection limits, the technician should review the instructions supplied with the test kit to verify that all steps were followed properly and ensure that reusable equipment and supplies used are properly decontaminated.
- **Duplicate analyses** are two analyses performed on the same sample. Duplicates are used to monitor the precision or reproducibility of the analytical technique and should be analysed at a frequency of one for every 20 regular samples. Care must be taken so that the samples are homogeneous before splitting for duplicate analysis otherwise the duplicate comparison will be unacceptable. The variation between the results should be consistent with the QA/QC requirements of the project or with the recommendations of the manufacturer of the test kit.
- **Precision** is a measure of the reproducibility of sample data between measurements and is affected by the homogeneity of the sample matrix, consistency of the test kit or technique used and user’s practice.
- **Accuracy** is a measure of how close an analysis comes to the "true" concentration in a sample.

There are several means of assessing the precision and accuracy of a test kit or field technique including:

- **Control samples** which are used to assess the accuracy of the operator, the method, and kit being used. The samples are solutions of known concentrations often supplied by the manufacturer. They are analysed with each set of calibration standards before analysis of the regular samples. The concentration in the control sample must fall within a specified range if the method is to be considered accurate. Third-party control samples having known concentrations of contaminants can be purchased for use with other reagent kits.
- **Confirmatory samples** are collected from the same sample that is analysed on site with the test kit but are sent to a laboratory off site for formal analysis. The results of the on-site analyses are compared with the results of the analyses by the off-site laboratory. The purpose of collecting confirmatory samples is to support proper interpretation of the results from the test kit and to judge the accuracy of the data from the standpoint of making correct decision making.

The same caveat applies to duplicate samples and confirmatory samples in that if care is not taken to ensure that samples are homogeneous before splitting for off-site analysis, the comparison between the test kit result and the confirmatory result will be unacceptable because of sample variability. The rate of confirmatory samples should be sufficient to allow for management of analytical uncertainty so that the use of the kit's data can be defended as scientifically valid. The rate of confirmatory samples will therefore vary from project to project depending on the kit, the complexity of the matrix being examined, how the data are being used, and the likelihood that interferences could be causing erroneous results. Confirmatory analysis should not be used as a substitute for proper QA/QC during test kit use. Many QC measures can be applied when using test kits, such as blanks, duplicate analyses, control samples, and carefully selected confirmatory analyses that build confidence that decisions at an action level are being made correctly. Confirmatory soil and water samples should be collected if it is necessary to provide definitive determination of contaminant concentrations in a sample.

Table 12: Calibration requirements and recommended quality assurance (QA) and quality control (QC) activities.

Instrument/ field test kit	Manufacturer	Technology	DQL	Recommended QA/QC
HAPSITE® INFICON® Inc	INFICON	Gas chromatography - mass spectrometry	Semi-quantitative to Quantitative	• Use internal standard gas as mass calibrator for compound identification and quantitation. • Calibration is required before every use and after 12 hours of operation. • Method blanks used to check the system.
Portable FLIR Griffin™ G510 GC/MS	FLIR	Gas chromatography - mass spectrometry	Semi-quantitative to Quantitative	• Use of internal standard gas as mass calibrator for compound identification and quantitation. • FC-43 (perfluorotrilamine) is often used as calibrant. • Method blanks used to check the system.
Torion T9 Perkin Elmer	Perkin Elmer	Gas chromatography - mass spectrometry	Semi-quantitative to Quantitative	• Calibration with Calion™ PV Mixes/ standards. • Auto mass calibration routine built into the instrument used for automatic calibration. • Method blanks used to check the system.
Environmental and BTEX GC systems SRI	SRI Instruments	Gas chromatography	Semi-quantitative to Quantitative	• Method blanks used to check the system. • Calibrant used is BTEX Plus standard. • As standard analytical practice, run a blank after a high concentration sample
FROG-5000™ Portable GC	Defiant Technologies	Gas chromatography	Semi-quantitative to Quantitative	• Calibration service is offered by the company at a cost. • BASS-100 automated calibration gas dilution system can be purchased from Defiant Technologies – lab setting. • A portable gas diluter is available to purchase from Defiant Technologies for gas calibration in the field, featuring 200:1 dilution capability using dilution air.
Handheld Flame ionization detector (FIDs) MicroFID II	Environmental Monitoring	Flame ionization	Semi-quantitative	• Typically calibrated with methane. • Minutes for daily field calibration check; up to one hour for full calibration and cleaning • Instrument should be zeroed in the atmospheric conditions where it will be used. • Calibration adjustments should be made in the field when measurements vary more than 10% from known calibration standard values • Response factors can be used to quantify compound specific concentrations.
Handheld Photoionization Detector (PID) MiniRAE,	RAE Systems / RKI Instruments	Photoionization	Semi-quantitative	• Typically calibrated with isobutylene standard • Minutes for daily field calibration check; up to one hour for full calibration and cleaning • Instrument should be zeroed in atmospheric conditions where it will be used. • Calibration adjustments should be made in the field when measurements vary more than 10% from known calibration standard values • Correction factors can be used to quantify different chemicals using only a single calibration gas containing a mixture of the relevant compounds.

Table 12 Cont'd

Instrument/ field test kit	Manufacturer	Technology	DQL	Recommended QA/QC
Infracal® TOG/TPH Analyser	Wilks Enterprise, Inc./ Spectro Scientific	Infrared spectrometry	Semi-quantitative to Quantitative	• Calibration using known standards. • Seven-point calibration for Model CVH and a five-point calibration for Model HATR-T. • Calibration standards for Models CVH and HATR-T were prepared by dissolving 3-IN-ONE oil in Freon 113 and Vertrel® MCA, respectively. • Zero calibration checks using blank solvent are also conducted at the beginning and end of each day and after analysis of every 10 samples.
ASD FieldSpec 4 Hi-Res Spectroradiometer	Malvern Panalytical	Visible near infrared spectrometry	Semi-quantitative to Quantitative	• Calibrations required for wavelength, absolute reflectance, radiance and irradiance. • All calibrations are NIST traceable (radiometric calibrations are optional). • Calibration is repeated at 30-minute intervals. • The white reference measurement aimed to avoid, and possibly remove, dark current and effects from variation in ambient temperature and humidity.
RemScan®	Ziltek	Mid-infrared FTIR spectroscopy	Semi-quantitative to Quantitative	• Air-dry sample and de-agglomerate as necessary, removing rocks and foreign material. • Create dilution series (14 samples ranging 100,000 mg/kg to 0 mg/kg). • Scan dilution series with RemScan® to collect spectra. • Due to the soil heterogeneity, the same soil sample needs to be scanned 5 times with mixing in between scans and then average the 5 readings. • Build a site-specific calibration model based on the IR spectra and theoretical TPH values and load model into RemScan® instrument. • Validate the calibration model by measuring validation samples.
4300 Agilent Handheld FTIR	Agilent	Mid-infrared FTIR spectroscopy	Semi-quantitative to Quantitative	• The system requires 30 min warm-up prior to calibration followed by a signal-to-noise test, a stability test and laser frequency calibration using Agilent validated software. • A background scan is usually performed to derive the baseline profile of the system without any sample.
QualitySpec Trek	Analytical Spectral Devices Inc.	Visible near infrared spectrometry	Semi-quantitative	• Additional calibration is made before every measurement occasion with a separate white reference plate. • Full-spectrum dark reference is measured also during the start-up with an internal shutter, the light source is turned off, and the white reference is plugged. The dark reference (background) value is subtracted from raw data prior to the reflectance calculation.
OCMA-350 Oil Content Analyser	Horiba Instruments, Incorporated	Infrared spectroscopy	Quantitative	• Automatic calibration after the calibration standard is introduced to the instrument.

Table 12 Cont'd

Instrument/ field test kit	Manufacturer	Technology	DQL	Recommended QA/QC
Analytical Test Kit UVF-3100A	SiteLAB Corporation	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• Calibrated using 5 calibration solutions to give a 5-point curve. The manufacturer provides calibration kits (each containing 5 standards) for gasoline range organics, diesel range organics, PAHs, and TPH.
Rapid Optical Screening Tool (ROST®)	Fugro	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The ROST® system is calibrated using reference emitter (RE). The RE is similar to a calibration gas used in a flame ionization or photoionization detector and is placed on the sapphire probe window before each push. • This measurement is a check of system performance and provides a means for normalizing measurements.
SCAPS LIF	Fugro	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The SCAPS LIF sensor's response is checked using a quinine sulphate fluorescent standard before and after each push. This measurement is a check of system performance and provides a means for normalizing measurements. • If the fluorescent intensity changes by more than 20% of the initial value determined during pre-push calibration, system troubleshooting procedures are initiated.
TarGOST®	Dakota Technologies	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The TarGOST® system is calibrated using a reference emitter
UV LED	Vertek Manufacturing	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The UV LED is calibrated using a dark and light card to ensure its output falls within an acceptable range.
UVOST®	Dakota Technologies	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The UVOST® system is calibrated using a reference emitter.
DyeLIF™	Dakota Technologies	Ultraviolet fluorescence spectroscopy	Qualitative to semi-quantitative	• The DyeLIF™ system is calibrated using a proprietary reference emitter.
Hanby TPH Soil kit	Hanby Environmental	Colorimetry	Semi-quantitative	• There is no calibration involved in the use of colorimetric indicator tubes. • The tubes are designed to produce an acceptable result if the appropriate volume of air is drawn through them, as required for each specific test.
Dräger Detector Tubes	Dräger	Colorimetry	Qualitative to semi-quantitative	• No calibration of detector tubes is required. All materials are provided pre-charged and ready for use. • Some analytes require the sample to be drawn through a dryer tube first, to remove moisture from the sample gas stream. • Operation may require multiple pump strokes, so a close fit between the detection tube and the sample container are required to minimize volatile losses during testing • Limited shelf life.
RaPID® Assay	Modern Water	Immunoassay	Qualitative to semi-quantitative	• Zero standard, wash, enzyme conjugate, colour development and stop reagents. • Standards for 0.09, 0.35 and 3.0 ppm as total BTEX. • Kit control as 2.1 ppm as total BTEX.

Table 12 Cont'd

Instrument/ field test kit	Manufacturer	Technology	DQL	Recommended QA/QC
PetroFLAG® test kit	Dexsil	Emulsion turbidimetry	Qualitative to semi-quantitative	• The meter can be calibrated using an extraction solvent vial as a blank and the calibration standard provided with the kit. • Equipment must be calibrated at a minimum frequency of one time per day, or approximately every 10 samples • Samples can be run individually or batched. • If the temperature varies by more than 10°C from the calibration temperature, the accuracy of the resulting measurement will be affected. Therefore, during each measurement made by the meter, the current ambient temperature is compared to the temperature determined at calibration. If the difference is more than 10°C, a warning is flashed alerting the operator of the temperature drift. • The PetroFLAG analyser stores two independent calibration equations in separate memory locations. Each calibration has a unique designation, "1C" or "2C". One way to effectively use this feature is to use one for a "low temp." calibration and one for a "high temp." calibration. This practice is very useful when working at field locations where the ambient temperature varies by more than 10°C over the course of the day.

2.4. ECONOMIC CONSIDERATIONS

Test kits and field technologies costs can vary significantly. Kit content, instrument design, accessories, and the quantity ordered will all affect the prices. Manufacturers / rental providers should be contacted directly for current cost information.

The relative cost information provided in **Table 13** is indicative and represented by one of the following designations: **€** which represent relatively low cost; **€€** which represent relatively medium cost; and **€€€** which represents relatively high cost. In comparison to fully quantitative laboratory analysis, which include direct costs for sample transport, handling, storage and disposal as well as (skilled) staff and instrument time and indirect costs (i.e. maintenance, parts and consumables), the relative cost will be higher than any of the categories used in the **Table 13**.

Table 13: Relative costs for equipment purchase, rental and sample analysis

Instrument/ field test kit	Equipment Purchase	Equipment Rental cost	Indicative cost per sample	Indicative cost for consumables
HAPSITE® INFICON® Inc	€€€	N.A.	€€ to €€€ if speciation required	€€ to €€€
Portable FLIR Griffin^{TM} G510 GC/MS	€€€	N.A.	€€ to €€€ if speciation required	€€ to €€€
Torion T9 Perkin Elmer	€€€	N.A.	€€ to €€€ if speciation required	€€ to €€€
Environmental and BTEX GC systems SRI	€€	N.A.	€€ to €€€ if speciation required	€€
FROG-5000™ Portable GC	€€	N.A.	€€	€€
Handheld Flame ionization detector (FID) MicroFID II	€	N.A.	€	none
Handheld Photoionization Detector (PID) MiniRAE	€	€/ month	€	none
ASD FieldSpec 4 portable spectroradiometer	€€	N.A.	€	none
RemScan®	€€	€/ week	€	none
4300 Handheld FTIR	€€	N.A.	€	none
QualitySpec Trek	€€	N.A.	€	none
OCMA-350 Oil Content Analyser	€	N.A.	€€	€€
Analytical Test Kit UVF-3100A	€	€€€/ day	€€	N.A.

Table 13 Cont'd

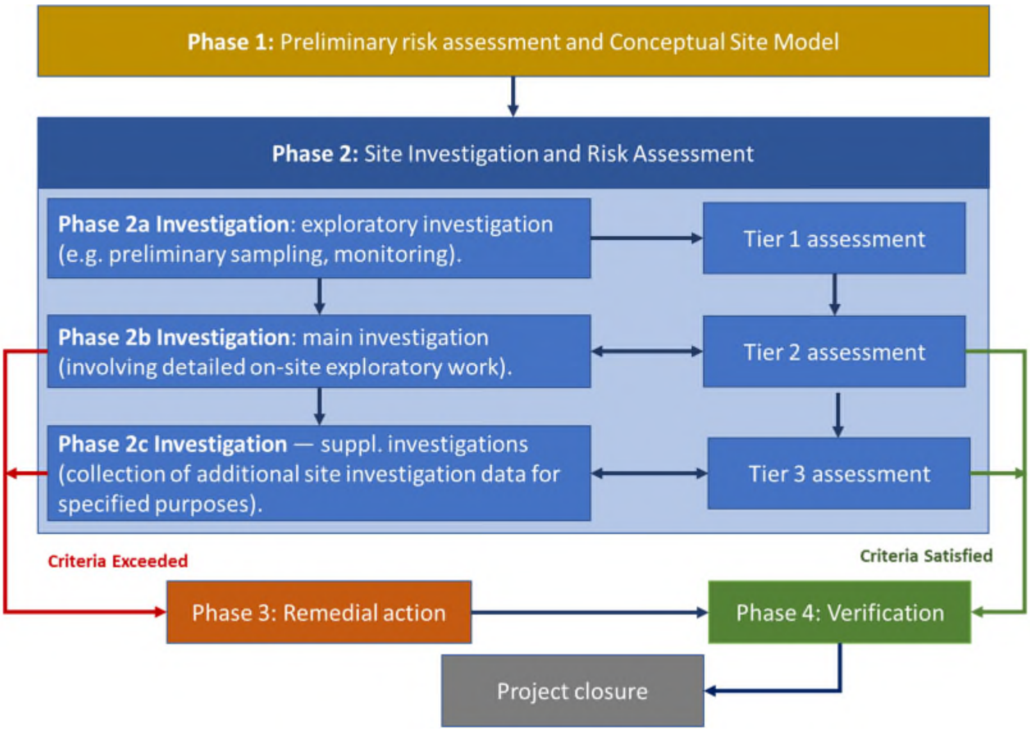
Instrument/ field test kit	Equipment Purchase	Equipment Rental cost	Indicative cost per sample	Indicative cost for consumables
Rapid Optical Screening Tool (ROST®)	N.A.	€€€/ day	N.A.	N.A.
SCAPS LIF	N.A.	€€€/ day	N.A.	N.A.
TarGOST®	N.A.	€€€/ day	N.A.	N.A.
UV LED	N.A.	€€€/ day	N.A.	N.A.
UVOST®	N.A.	€€€/ day	N.A.	N.A.
DyeLIF™	N.A.	€€€/ day	N.A.	N.A.
Hanby TPH Soil Kit	€	N.A.	€€	€€
Dräger Detector Tubes	€	€/week	€	€
RaPID® Total BTEX/TPH 100 tube kit	€	N.A.	€€	€€
PetroFLAG® test kit	€	N.A.	€€	€€

Key: N.A. – not applicable

3. REGULATORY REQUIREMENT FOR FIELD ANALYTICAL TECHNOLOGY DEPLOYMENT AND SITE INVESTIGATION

Before embarking on any phase or stage of investigation (**Figure 3**), it is important to set data quality objectives in terms of the type, quantity and quality (e.g. analytical quality) of the data and other information that have to be collected. These data quality objectives will depend in part on the nature of the decisions to be made on the basis of the investigation, and the confidence required in those decisions. When deciding on the strategy, consideration should be given to the applicability and use of on-site analysis and/or in situ measurement techniques. Guidance on the selection and application of on-site methods is provided in ISO 12404:2015.

Figure 3: Overview of the phased site investigation process (Tier 1: Generic risk screening; Tier 2 Simple quantitative risk assessment; Tier 3: Detailed quantitative risk assessment)



- **Phase 1 Site Investigation** or Preliminary Risk Assessment (Desk Study) is an integral and founding part of the site investigation process. It is used to create a preliminary Conceptual Site Model (CSM) in order to identify any potential pollutant linkages at a site. The CSM will enable a preliminary risk assessment to be made which will indicate whether a Phase 2 investigation is required. The CSM should be reviewed and revised through the subsequent phases as more information is gathered.
- **Phase 2 Site Investigation and Risk Assessment** is the second stage in the site investigation process, where the results and recommendations presented in the Phase 1 Desk Study outline the requirement for further investigation. This is usually a ‘preliminary investigation’ by way of intrusive ground investigation using a combination of various techniques depending on the potential risks

identified during the Phase 1 Desk Study. The Phase 2 Site Investigations are designed to collect information on a site as a whole for both geo-environmental and geotechnical purposes, and therefore an overview of the intended sampling including information and justification of sample locations, depths, patterns and numbers and the frequency and duration of sampling or monitoring to be undertaken is required. The analytical methods that will be used should also be mentioned and independently accredited laboratories should be used to carry out analysis. The use of in-situ testing and rapid measurement techniques during Phase 2 is also accepted as it can reduce the cost of both site investigation and remediation (Phase 3) (e.g. Environment Agency's Position Statement 307_03, 2016 - Chemical Test Data on Contaminated Soils – Qualification Requirements, Position (Environment Agency, 2019)).

- **Phase 3 Remediation and Phase 4 Validation:** If Phase 2 identifies any unacceptable risks, then Phase 3 (known as remediation) will be required. Remediation is the act of rendering a site 'fit for purpose' and the Phase 4 validation, also known as Verification, is the process by which the evidence is gathered and presented to verify that the proposed and agreed upon remediation strategy has been achieved. These phases typically require contaminants monitoring to validate remedial action has been successful and confirmed in post-treatment management. Analytical results for all verification samples should be reported with a detailed comparison and interpretation against the remediation criteria, which were agreed in the remediation strategy.

Among the field analytical techniques currently available and reviewed in this report, field fluorescence systems (i.e. fibre optics, laser induced fluorescence) are typically used for in-situ petroleum hydrocarbons measurements without the need of sample extraction. Field spectrometry technologies allow both direct in-field measurements and in on-site laboratory measurements. Spectroscopy is a non-destructive technique and does not required any sample extraction.

For the other technologies including gas chromatography systems, photo- and flame-ionizations detectors, detector tubes, immunoassay tests, colorimetric and turbidimetry kits, they all required either a sample extraction using chemical solution or thermal desorption (i.e. for PID and FID detectors) before analysis. They are therefore classified as ex-situ petroleum hydrocarbons analysis that can be conducted either in on-site laboratory or in-field measurements.

Based on the data quality levels provided by each field analytical technology reviewed in this report, an indication of their relevance and use for Phase 2 to Phase 4 site investigations is summarised in **Table 14**.

Table 14: Field analytical technologies relevance for the site investigation phases

Analytical technique	Instrument/ field test kit	Measurement		Sample solvent extraction	Phase 2			Phase 3	Phase 4
		Direct in-field	**On-site lab**		2a	2b	2c		
Gas chromatography coupled to mass spectrometry	HAPSITE®	✓	✓	Yes		✓	✓	✓	✓
	FLIR Griffin^{TM} G510	✓	✓	Yes		✓	✓	✓	✓
	Torion T9 Perkin Elmer	✓	✓	Yes		✓	✓	✓	✓
	Environmental and BTEX GC SRI	✓	✓	No		✓	✓	✓	✓
	Frog-5000	✓		No		✓	✓	✓	✓
Ionization	FID MicroFID II	✓		No	✓	✓		✓	
	PID MiniRAE, RKI Eagle 2	✓		No	✓	✓		✓	
Spectroscopy	Infracal® TOG/TPH Analyser		✓	Yes	✓	✓		✓	
	ASD FieldSpec 4 Hi-Res	✓	✓	No	✓	✓		✓	
	RemScan®	✓	✓	No	✓	✓		✓	
	4300 Agilent Handheld FTIR	✓	✓	No	✓	✓		✓	
	QualitySpec Trek	✓	✓	No	✓	✓		✓	
	OCMA-350 Oil Content Analyser		✓	Yes	✓	✓		✓	
Fluorescence	Analytical Test Kit UVF-3100A		✓	Yes	✓	✓		✓	
	ROST®	✓		No	✓				
	SCAPS LIF	✓		No	✓				
	TarGOST®	✓		No	✓				
	UV LED	✓		No	✓				
	UVOST®	✓		No	✓				
	DyeLIF™	✓		No	✓				
Colorimetry	Hanby TPH Soil kit		✓	Yes	✓	✓		✓	
	Dräger Detector Tubes	✓		No	✓	✓			
Immunoassay	RaPID® Assay		✓	Yes	✓	✓		✓	
Turbidimetry	PetroFLAG® test kit		✓	Yes	✓	✓		✓	

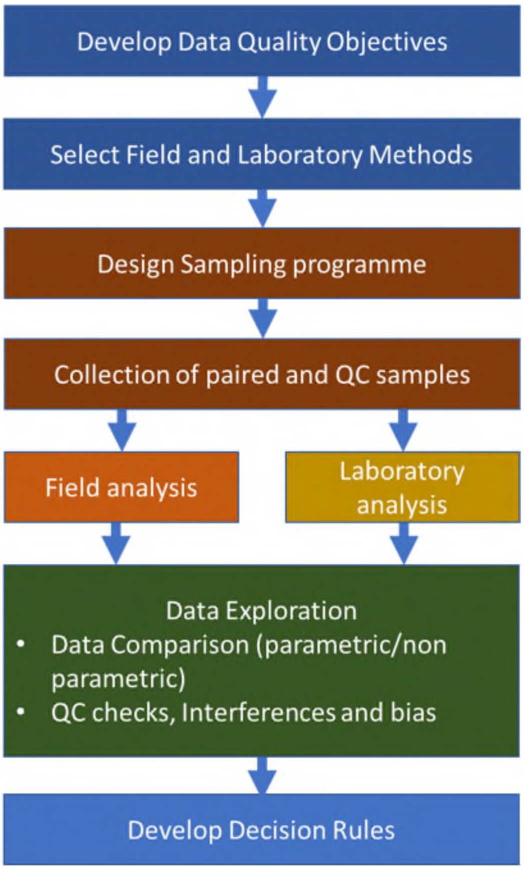
Key: **Phase 2a** Rapid measurement, Qualitative to semi-quantitative allowing soil mapping for hot spot detection and determination of presence and absence of hydrocarbons. **Phase 2b** Semi Quantitative to Quantitative information on presence of petroleum hydrocarbons ranges and concentrations. **Phase 2c** Quantitative information on petroleum hydrocarbons composition and concentrations. **Phase 3**: Semi Quantitative to Quantitative information on petroleum hydrocarbons reduction over time. **Phase 4**: Quantitative information on petroleum hydrocarbons composition and risk indicators compounds reduction end point.

It should be however noted that petroleum hydrocarbons characterisation and quantification in soil, is a challenging task due to the vast complexity of petroleum compounds having different solubility and volatility (Coulon and Wu, 2014).

From a risk assessment point of view, it is indeed desirable to gather information about the amount of different hydrocarbon compounds preferably differentiating between aliphatic and aromatic fractions, and at the moment this can only be achieved by means of gas chromatography-mass spectrometry. Also when a petroleum product is released into the soil, the most volatile fractions volatilize into the air within a relatively short period of time (approximately a month), followed by the migration of the remainder through the soil and either reaching the groundwater for the more water-soluble compounds (i.e. BTEX) or adsorbing onto soil solids for the heavier compounds (i.e. 3-, 4- and 5-ring PAHs) (Bajagain et al., 2020; Wang et al., 2019; Xiao and Zytner, 2019). Therefore, the diverse factors affecting ageing of petroleum hydrocarbon contaminants in soil will introduce some variability to the sampling and the analysis process and therefore the selection of the field analytical technologies.

Furthermore, to ensure collected data will meet appropriate quality standards, the use and deployment of field technologies will require conducting a demonstration of method applicability (DMA), similar to those developed by the U.S. EPA under its Brownfields Initiative (U.S. EPA, 2008) or the Environment Agency's framework for risk management of land contamination in England (Barnes, 2009; Environment Agency, 2018). DMA is a site-specific performance evaluation which compares data from the field technique to data obtained in laboratory by a certified method. For example in the case of the Environment Agency's framework for risk management of land contamination in England, field measurements are compared against results obtained by a certified laboratory under the Environment Agency's Monitoring Certification Scheme for Chemical Testing of Soil (Environment Agency, 2018). The data comparison involves (i) determining the distribution of the sample population (e.g. normal, lognormal, or other); and (ii) finding the mathematical relationship between data sets (e.g. correlation scatter plots, best-fit lines). While designing a DMA is an open process without a generic format, the most common steps are illustrated in **Figure 4.**

Figure 4: Design of a demonstration of analytical technology applicability



To demonstrate that a less-sophisticated method correlates well with a standard method, a linear regression is the most common approach in a DMA. The laboratory data is considered as a surrogate of the true value measurement, whereas results from the field method represent estimated measurements. The goodness of the fit should be determined by checking the slope, y-intercept, and regression coefficient. For sampling purposes, a DMA requires 20 or fewer field paired samples (e.g. linear regression require at least 10 paired samples), though the final number depends on the magnitude of the site. Sample pairs should target decision levels, for instance 5 low values, 5 high values, and 10 in areas around action levels. Additionally, uncertainties affecting the overall measurement error should be established by including sample and analytical duplicates (precision) and certified reference materials (bias).

4. CONCLUSIONS

Overall, the state of development of the field analytical technologies for petroleum hydrocarbons determination in soil is mature and well established. From a risk assessment point of view, GC-MS is the only technique currently capable of discriminating quantitatively between the aliphatic and aromatic petroleum fractions. However, they require soil sample extraction and a high level of expertise which may not suit all project needs.

In contrast, colorimetric, immunoassay and turbidimetry test kits can all offer rapid and cost-effective means for monitoring petroleum hydrocarbons decrease overtime and inform the remediation strategies. However, they do not give information on specific analytes and tend to be specific or sensitive to certain hydrocarbon groups or hydrocarbon banding ranges.

Field spectrometry technologies offer real-time measurement of petroleum hydrocarbons concentrations in soil that can expedite an on-the-go assessment (typically within 20-30 seconds). They require minimal sample handling and preparation but are sensitive to high soil moisture (typically >5% free moisture content). Soil drying would therefore be required before analysis which will influence the hydrocarbons analysis determination, especially petroleum hydrocarbons ranging between EC_{10}-EC_{12}. Furthermore, infrared spectroscopy technologies do not discriminate between the fraction of interest (i.e. aliphatic /aromatic fractions) and are subject to interferences caused by non-hydrocarbon compounds that also contain C-H bonds that absorb (overlap) at the same wavelength. As a result, complex chemometric processes including multivariate statistical methods are needed for the interpretation of the spectra, which require the user to have a reasonable understanding and knowledge of chemometrics and programming.

Fluorescence technologies tend to be used for in-situ site investigation providing high level spatial resolution of hydrocarbons contamination in soil. However, fluorescence systems provide relative data rather than quantitative data and they all require highly skilled personnel.

Nevertheless, both spectrometry and fluorescence systems can be part of an adaptive sampling design whereby sampling efforts are directed to areas of concern making the detection of petroleum hydrocarbons in soil easier and faster, and therefore allowing higher resolution of contamination levels predictions during the Phase 2 Investigation.

Finally, it is important to acknowledge that there is currently not a single field analytical technology that allows to determine and quantify the entire range of petroleum hydrocarbons in soil and therefore a combination of analytical technologies (i.e. combining PID with vis-NIR or GC-MS with vis-NIR) has the potential to offer a more robust approach in quantifying petroleum hydrocarbons in soil by providing greater prediction accuracy.

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6. LIST OF ABBREVIATIONS

AC	Alternating Current
AMDIS	Automated Mass spectral Deconvolution and Identification System
AMU	Atomic Mass Unit
APCI	Atmospheric Pressure Chemical Ionization
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CLU-IN	Contaminated Site Clean-Up Information
CPT	Cone Penetrometer
DC	Direct Current
DL	Detection Limit
DNAPL	Dense Non-Aqueous Phase Liquid
DP	Direct Push
DQL	Data Quality Levels
DRIFT	Diffuse Reflectance Infrared Fourier Transform
DTGS	Deuterated Triglycine Sulphate
DyeLIF	Dye-Enhanced Laser Induced Fluorescence System
ECIA	Electrochemical Immunoassay
EDRO	Extended Diesel Range Organics
EI	Electron Ionization
ELISA	Enzyme-Linked Immunosorbent Assay
EPA	Environmental Protection Agency
ESI	Electrospray Ionization
FC-43	Perfluorotributylamine
FIA	Fluorescence Immunoassay
FID	Flame Ionization Detection
FOCS	Fibre Optical Chemical Sensors
FT	Fourier Transform
FT-ICR	Fourier Transform Ion Cyclotron Resonance
FTIR	Fourier-Transform Infrared Spectroscopy
GB	Great Britain
GC	Gas Chromatography
GC-FID	Gas chromatography with Flame Ionization Detection
GC-MS	Gas Chromatography Mass Spectrometry
GLP	Good Laboratory Practice
GPS	Global Positioning System
GRO	Gasoline Range Organics

HPLC	High-Performance Liquid Chromatography
IMA	Immunoassay
IR	Infrared
IS	Imaging Spectroscopy
ISO	International Organization for Standardization
LCD	Liquid-Crystal Display
LIBS	Laser-Induced Breakdown Spectroscopy System
LIF	Laser-Induced Fluorescence
MAH	Monocyclic Aromatic Hydrocarbons
MDL	Method Detection Limit
MIR	Mid-infrared
MS	Mass Spectrometry
MSD	Mass Selective Detector
MTBE	Methyl tert-butyl ether
NAPL	Non-Aqueous Phase Liquid
NDIR	Nondispersive Infrared
NEG	Non-Evaporative Getter
NIR	Near-Infrared
NIST	National Institute of Standards and Technology
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PDA	Personal Digital Assistant
PHC	Petroleum Hydrocarbon
PID	Photoionization Detection
PPB	Parts-per-billion
PPM	Parts-per-million
PPM	Parts-per-million
PPT	Parts-per-trillion
PSR	Penalized Spline Regression
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QC	Quality Control
RFR	Random Forest Regression
RH	Relative Humidity
RIA	Radioimmunoassay
ROST	Rapid Optical Screening Tool

RPD	Regression Point Displacement
RSME	Root-Mean-Square Error
SCAPS	Site Characterization and Analysis Penetrometer System
SDI	Strategic Diagnosis Incorporated
SIM	Selected Ion Monitoring
SOM	Soil Organic Matter
SPME	Solid Phase Micro Extraction
SVOC	Semi-Volatile Organic Compounds
SWIR	Short-Wave Infrared
TarGOST	Tar-Specific Green Optical Screening Tool
TMS	Toroidal ion Trap Mass spectrometer
TPH	Total Petroleum Hydrocarbon
TVOC	Total Volatile Organic Compounds
US	United States
USA	United States of America
UV	Ultraviolet
UV LED	Ultraviolet Light Emitting Diode
UVF	Ultraviolet Fluorescence
UVOST	Ultraviolet Optical Screening Tool
VIRS	Visible and Infrared Reflectance Spectroscopy
VIS	Visible
Vis-NIR	Visible and near-infrared
VOC	Volatile Organic Compounds
WR	White Reference
WTM	Wavelength/Time Matrix
XRF	X-Ray Fluorescence Spectrometry

7. ACKNOWLEDGEMENT

This report is one of the outputs of Concawe Soil and Groundwater Special Task Force (WQ/STF-33) on TPH Field Screening Methods to evaluate and raise awareness of the field-based techniques available to determine petroleum hydrocarbons concentrations in soil and determine whether they can provide a reliable alternative to sending all samples to a laboratory for analysis. The objectives are to provide an overview of the different techniques reflective of the full range available; from the high-end field gas chromatographs and handheld infrared spectrometers to field chemical kits that create a colorimetric response, to low-end oil pans.

The report was prepared by Célia Lourenço, Pablo Campo, Chris Walton, Maria Carmen Alamar and Frederic Coulon (Cranfield University).

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APPENDIX 1

The Appendix contains the following supplemental information:

1. Details on the literature review strategy and respective search string combinations, and the total number of documents retrieved per screening stage.
2. Detailed description of the principle of each analytical technique, and the operation of the different technologies covered in each field-based technique along their respective advantages and limitations.

A1.1 LITERATURE SEARCH METHODOLOGY

Table A.1 Search strings combinations and total number of documents selected per screening.

Scopus database search strings	Total number of articles	Number selected on 1st screening (title and abstract)	Number selected for the report (full text)
(A) String 1 + string 2	681	120	16
(B) String 1 + string 3	49	27	9
(C) String 2 + string 3	9	5	0*
(D) String 1 + string 4	21	13	4
(E) String 1 + string 2b	1948 (Limited to years 2020-2018): 409	55	8
		Total no. of documents	
Regulators (ISO, EPA)		16	
Manufacturers websites/ brochures		18	
Books		3	
General Google search		8	
TOTAL		**82**	

* to avoid duplication of documents.

String 1: "tph" OR "Tph contamination" OR "phc contamination" OR "total petroleum hydrocarbons" OR "petroleum hydrocarbon" OR “soil tph”

String 2: “soil contamination” OR “soil remediation” OR “soil testing”

String 2b: “soil contamination” OR “soil remediation” OR “soil testing” OR “contaminated soil”

String 3: “field test kits” OR “field screening tools” OR “tph analysis” OR “tph screening devices” OR “soil screening technology”

String 4: “handheld” OR “field testing” OR “hand-held”

The key steps taken for sourcing and screening the articles were as follows:

1. A selected number of relevant keywords/ search strings were identified.
2. Five search string combinations were used, and the total number of articles was recorded for each combination of search strings. The search strings combinations significantly improved the number of ‘hits’.
3. The search string combination “string 1 + string 2b” was created since the search string combination “string 1 + string 2” failed to identify the most recent and relevant literature. Therefore “string 1 + string 2b” was created and limited to the publication year between 2020-2018 to restrict to the most recent advances within the field.

4. All the remaining search strings were not restricted to publication year or any other restrictions.
5. The total number of articles 681, 49, 9, 21 and 409, correspondent to the search strings (A), (B), (C), (D) and (E), respectively, was retrieved from the database and recorded accordingly.
6. At the first screening stage, articles were included/excluded based on the title and abstract retrieved from the database. The number of articles selected on the first screening was recorded accordingly. This process was performed for each combination of search strings. At the first screening 120 articles were selected for search string (A), whereas 27, 5, 13, and 55 articles for (B), (C), (D) and (E), respectively.
7. The respective full text of the articles selected at the first screening was extracted from the database and read accordingly. Duplicate articles were managed accordingly, and relevant articles were noted. A total number of 16 articles were selected for search string (A), whereas 9, 0, 4, and 8 articles for (B), (C), (D) and (E), respectively.
8. The relevant articles were selected, and the numbers recorded accordingly.
9. Three books were accessed and included in this review.

Targeted grey literature search of specific web sites from key organisations was also conducted, including:

a) Regulators: U.S. Environmental Protection Agency (EPA), the International Organization for Standardization (ISO), Environment Agency of England: a total of 16 documents were retrieved from these particular organisations.
b) Manufacturers websites and product brochures: a total of 18 documents was retrieved.
c) Wider internet using a general-purpose search engine (Google) and a total of 8 documents was retrieved.

A1.2 PRINCIPLES OF EACH ANALYTICAL TECHNIQUE

A1.2.1 Gas Chromatography

Typical characterisation of TPH soil contamination commonly relies on expensive regulatory approved laboratory-based techniques and time-demanding analytical methods for quantitively determine total petroleum hydrocarbons in soil. The most common approach used for elucidation of the structural composition and quantification of volatile mixtures such as TPH, consists in solvent extraction of the matrix and subsequent analysis by gas chromatography (GC).

In general, gas chromatography allows the analysis of complex mixtures of compounds through a separation step in a capillary column subjected to a temperature profile inside a temperature-controlled oven. In the column compounds separate according to the relative affinity for the stationary phase of the column and elute at different retention times being further detected respectively. Most environmental hydrocarbons are volatile and thermally stable; therefore, these can easily be analysed by gas chromatography. In gas chromatography, the sample is evaporated and carried through the column by an inert carrier gas typically helium, known as the mobile phase. Not only is helium more cost-effective but also because it combines a faster separation and safety of operation once compared to hydrogen (Gross, 2017).

Typically, the soil sample is injected in the column as an extracted solution in a volatile solvent. However, solvent extraction yields can be strongly matrix dependent, e.g. interactions between soil components, pollutants, soil organic matter, therefore having a significant impact on solid-liquid extraction. The solvent extraction is also dependent on the moisture content in the soil (Schwartz et al. 2012). Extraction processes such as Soxhlet, microwave or ultrasonic extraction method are the most commonly used (Coulon and Wu, 2014; Imam et al., 2019).

The coupling of a chromatograph with highly sensitive detectors such as flame ionization detection (FID) and mass spectrometry (MS) makes it ideal for the analysis of sensitive petroleum hydrocarbons with very high sensitivity and specificity (Douglas et al., 2017). The hyphenated techniques GC-FID, two-dimensional GC×GC-FID and GC-MS are the most commonly used in the analysis of TPH contaminated soil, and these are described in detail below. GC analysis with photoionization detection (PID) has been used extensively to characterise and remediate sites contaminated with volatile organic chemicals (VOCs).

Field gas chromatographs commercially available include HAPSITE® portable gas chromatograph-mass spectrometer, Torion T-9 Portable GC/MS Perkin Elmer and Portable FLIR Griffin™ G510 GC/MS.

Advantages	Limitations
• The optimised chromatographic method features the ability to separate, identify and accurately quantify volatile species using calibration standard mixtures. • Allows separation and identification between aliphatic and aromatic fractions. • Enhanced sensitivity and resolution. • Field GC can provide "real-time", or near real-time data, facilitating decision making and reducing the length of field mobilisation.	• Solvent extraction is required, and solvent extraction yields can be strongly matrix dependent. • Time-demanding analytical methods for determination of TPH in soil. • Typically, the complexity of the resulting chromatogram requires it to be examined by a specialist – high degree of expertise required. • Costly.

Mass Spectrometry

The coupling of a separation technique such as gas chromatography (GC) to mass spectrometry (MS) allows enhanced level of selectivity and sensitivity, and compounds to be resolved by unit mass resolution. This is true because a mass spectrometer is employed as the chromatographic detector. Thus, making it the mostly preferred technique for TPH analysis in petroleum contaminated soil (Okparanma et al., 2014).

Overall a mass spectrometer consists of an inlet, an ion source, a mass analyser, a detector, a high-vacuum system and an acquisition system. The signal measured on a GC-MS instrument derives from the ionization and fragmentation of molecules and is compound-dependent, thus it plays an important role in structure elucidation of hydrocarbon fractions. Accordingly, the compound-dependent ionization efficiency employed to deliver the ions to the mass analyser may vary considerably, consequently, chemical standards are important for careful instrument calibration and for determining the compound-dependent ionization efficiency of molecules. For quantitative purposes, the instrument's response versus the sample concentration will lead to absolute quantification of compounds, while relative signal intensities are used for a qualitative analysis. The separation of compounds is carried out in the GC column and the outlet gas sample is forwarded into the ion source of the mass spectrometer through a heated interface. In the ion source of the mass spectrometer, the ionization – electron ionisation (EI) is used in conjunction with GC – is achieved after collision of the gas sample with an electron beam of typically +70 eV, producing positively charged ions respectively. The high energy employed largely exceeds the first ionization energies of all organic compounds, thus the molecular ion undergoes several fragmentation reactions either by elimination of a radical or a molecule, producing accordingly numerous fragment ions. The resulting fragmentation pattern featured in the mass spectra is a fingerprint of the molecule under study (Gross, 2017). Therefore, aliphatic hydrocarbons and PAHs are accurately identified and quantified through the analysis of the mass spectra of the molecules (Douglas et al., 2018). The mass spectra of molecules are then compared against a mass spectral database, such as NIST/EPA/NIH or Wiley, where a compilation of thousands of EI mass spectra acquired at +70 eV is found. This provides a reproducible level of comparation among tests and between instruments, when standard operating conditions are employed, i.e. +70 eV, ion source 150 ¤C – 250 ¤C, pressure in order of 10^{-4} Pa.

The GC-MS response has been widely used recently in investigating the performance of many spectroscopic techniques in TPH contaminated soil. In many cases, the infrared response has been found to correlate significantly to TPH concentration acquired by GC-MS (Chen and Tien, 2020; Douglas et al., 2019b). There is evidence that GC-MS often lacks enough chromatographic resolution and mass resolving power to characterise the heavy hydrocarbon fraction (> C_{44}) (Brown et al., 2017). Other mass spectrometric techniques are better suited for this analysis, such as Fourier transform ion cyclotron resonance (FT-ICR). Fourier transform ion cyclotron resonance (FT-ICR) coupled with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) offers the highest mass resolving power and mass accuracy amongst all types of mass spectrometers and provides a better understanding of the composition of petroleum products and their degradation metabolites (Brown et al., 2017; Luo and Schrader, 2020). However, the addition of a high-resolution mass analyser significantly increases both instrumentation and maintenance costs.

Advantages	Limitations
• Using full scan mode, samples can be surveyed in a single analysis for the presence of a broad spectrum of organic chemical compounds. • Field portable or transportable GC-MS analysis can be of equal quality as fixed laboratory data. • Rapid analysis provides data that can be used to enable field decision-making, expediting clean-up or characterisation. • Mass spectrometry employed as the chromatographic detector can provide definitive compound identification and is the key difference from other detectors.	• Instrumentation is expensive. • Instrumentation operation requires a higher degree of expertise than most other instrumentation. • Full scan mode for the full range of compounds cannot produce the analytical accuracy and sensitivity possible with selected ion monitoring (SIM) considering a quadrupole mass analyser, which is the most commonly used.

GC×GC

A well-known limitation of GC-FID technique is the lack of chromatographic resolution of hydrocarbon fractions with boiling points above 200 ¤C (Imam et al., 2019). Thus, comprehensive gas chromatography, commonly known as GC×GC, is useful for the separation of heavier hydrocarbon fractions. The GC×GC instrumentation employs a serial connection of two columns, where the first column is about 20-30 times longer than the second. When columns of different polarities are used results in an improved separation of co-eluting compounds from the first to the second-dimension column, and this is known as two-dimensional gas chromatography (Gross, 2017). This multi-column technique is particularly useful for the separation of unresolved petroleum hydrocarbon signals, typically boiling points above 200 ¤C (Imam et al., 2019). For the characterisation of unresolved petroleum hydrocarbons, a non-polar column is typically used in the first dimension – separation through boiling point differences – and the eluted compounds are forwarded to a second-dimension polar column, ultimately leading to separation of aliphatic and aromatic hydrocarbons through polarity (Van De Weghe et al., 2006). The high separation power that GC×GC offers is an extraordinary advantage compared to a single GC column. The use of a GC×GC system is limited to locations that include field laboratories.

Advantages	Limitations
• GC×GC offers better sensitivity than conventional 1D. • Improved separation of unresolved petroleum hydrocarbon signals. • Useful for the separation of heavier hydrocarbon fractions. • Allows more reliable peak identification.	• Method development can be more complex. • Training required for instrumentation operation and data analysis. • Time-demanding methodology.

A1.2.2 Ionization detectors

A variety of detectors for gas chromatographs are available. In general, each detector takes advantage of a unique characteristic of a molecule and uses that characteristic to generate a measurable electrical signal.

Flame ionization detector

Flame ionization detection (FID) is the most common detector used in gas chromatography and for the quantification of TPH. Gas chromatography with flame ionization detection (GC-FID) is highly popular in TPH quantitative analysis due to its sensitive response to compounds that contain carbon atoms (organic compounds) but not to air, water, or light gases. However, FIDs are more sensitive to aliphatic (or chained) hydrocarbons because these compounds burn more efficiently than aromatic (or ringed) hydrocarbons (US EPA, 2016). The GC-FID system presents low detection limit (10 mg/kg) for TPH analysis in soil, fast and linear response over a very wide concentration range (Douglas et al., 2017). For many years, GC-FID has been the chosen analytical technique for the analysis of TPH in soil and has been widely used to assess landfarming and bioremediation processes in soils contaminated with petroleum hydrocarbons (Lee and Gongaware, 1997; Poi et al., 2017; Sanscartier et al., 2009; Zubair et al., 2015). The standard regulatory GC method for the analysis of TPH is EPA method 8015 (US EPA 2007) although the volatile compounds (gasoline fraction) should be extracted by headspace using EPA 5021A method (US EPA 2003). The Standard ISO 16703 is another standard method acknowledged for the determination of TPH concentrations from hydrocarbons with a boiling range of 175°C to 525°C – C10 to C40 – including saturated, cyclic, and aromatic hydrocarbons, except polycyclic aromatic hydrocarbons (PAHs) (ISO, 2004). Considerable improvements in GC method development are shown in a methodology for capturing the heavier fractions C_{34} – C_{50} using GC-FID (Zubair et al., 2015). Recent instrumental advances in pressure control and high-frequency FID detectors have emerged and led to the use of reduced capillary columns (2–10 m length and 0.1–0.05 mm internal diameter). Thus, providing greater analytical frequency and shorter analysis time, without impairing the chromatographic resolution. The methods are commonly known as ultra-fast GC (Nespeca et al., 2019). Numerous research groups have investigated and validated the response of portable devices against the GC-FID response and in many cases, the portable device's response has been found to correlate significantly to TPH concentration acquired by benchtop GC-FID instrumentation (Kong et al., 2017; Webster et al., 2016).

Photoionization detector

Photoionization detector (PID) is most sensitive to unsaturated compounds (e.g. BTEX compounds) and chlorinated hydrocarbons. The PID is a non-destructive detector that can be used in series before other detectors. Using multiple detectors extends the range of compounds that can be detected in one analysis. PID is sensitive to humidity and may require frequent recalibration.

Advantages	Limitations
• High sensitivity and fast response time. • Portable and relatively low cost. • Low skill/ training levels required for use. • PID can detect VOCs (aromatic and chlorinated) and petroleum constituents including benzene, toluene, ethylbenzene and xylene (BTEX). • FID response factors between aliphatic and aromatic hydrocarbons are essentially the same, making it equally adequate to analyses either group of organic compounds. • FID more sensitive to aliphatic compounds than PID. • FID Less sensitive to humidity than PIDs	• PID/FID do not detect compounds selectively. • PID cannot detect many aliphatic compounds • Cross-reactivity to many volatile hydrocarbons. • FID provide semi-quantitative results only which is typically referenced to isobutylene.

A1.2.3 Spectroscopy

The optical measurements made by the spectroscopic techniques involve absorbance, reflectance, or fluorescence of energy by petroleum hydrocarbons. Some of the devices use light in the visible wavelength range, such as colorimetry, and others work outside that region of the electromagnetic spectrum, e.g. infrared (IR), ultraviolet (UV). Detailed description of available technologies is below.

Advantages of IR Systems	Limitations of IR Systems
• An FTIR system consistently scans the infrared spectrum in fractions of a second throughout its optical range. • Very useful where fast, repetitive scanning is needed. • The system simultaneously measures all wavelengths. Scans are added. The signal is N times stronger; noise is N1/2 as great, and therefore the signal-to-noise advantage is N1/2. • There are no slits or gratings, thus energy throughput is high, and more energy is at the detector where it is needed most. • Near real-time data collection and reporting can be achieved. • Archived data can be re-analysed for new compounds. • The generation of a path-integrated concentration yields contaminant information along the entire path length and not just at a single point, so there is less chance of missing a plume. • Compound speciation of any compound with an IR absorbance can be obtained. • No sample collection, handling, or preparation is necessary. • FTIR provides cost effectiveness versus multiple discrete sampling points with separate analysis. • The system can be used to calculate the total flux of contaminants escaping from a facility.	• The minimum detection limits are influenced by factors such as water vapour, CO_2 concentrations, path length, and chemical interferences. • The signal can be reduced in several ways: beam divergence; atmospheric absorption due to water and scattering of the IR source from particulates; misalignment due to operator error, wind, or temperature; and beam blocks by pedestrians, vehicles, and buildings.

Infrared (IR) spectroscopy

The electromagnetic spectrum covers a range of frequencies at different wavelengths. The infrared (IR) region is a small portion of the electromagnetic spectrum and is divided into three regions including **near-infrared** (14000 - 4000 cm^{-1} or 750 - 2500 nm), **mid-infrared** (4000 - 400 cm^{-1} or 2500 - 25,000 nm) and **far-infrared** (400 - 10 cm^{-1} or 25,000 - 1,000,000 nm). In IR spectroscopy, molecules absorb radiations in the infrared region of the electromagnetic spectrum and occurs due to vibrational and rotational energy changes. Carbon-hydrogen bonds present in complex petroleum hydrocarbon mixtures are measured through the stretching and bending mode of vibration producing unique spectra of hydrocarbon compounds characteristic of a particular molecule (Douglas et al. 2017; Yadav et al., 2005). Regardless of the length of the carbon chain of molecules, all petroleum hydrocarbon fractions have similar band patterns in infrared spectral analysis. Infrared absorption bands at locations from 3000 to 2800 cm^{-1} represent carbon-hydrogen bonding for long-chain alkanes due to –C–H stretching vibrations, and a band at 730 cm^{-1} is exclusive to long-chain alkanes (Wang et al., 2019). Methyl groups CH_3 and CH_2 methylene have two infrared absorption bands each at approximately 2958 cm^{-1} and 2876 cm^{-1}, and 2924 cm^{-1} and 2864 cm^{-1} respectively (Dumitran et al., 2009). The analysis cost and time of IR methods are typically far less once compared to GC or HPLC techniques. A number of studies have investigated the use of infrared technologies for the rapid detection and assessment of total petroleum hydrocarbons (TPH) concentration in soil (Nespeca et al., 2018; Ng et al., 2017; Wang et al., 2019).

Advantages	Limitations
• Measurement of multiple chemicals at one time; • Large linear range. • Fast detection of hydrocarbons	• Often fail to determine and quantify the entire range of petroleum hydrocarbons in soil or sediment. • IR technologies do not discriminate between the compound of interest and any contaminants that absorb at the same wavelength in soil; • IR spectroscopic determination of TPH concentrations in soil requires a sample extraction step and subsequent analysis of the extracted TPH, which is not suitable for in-field application.

Visible and near-infrared (vis-NIR) and mid-infrared (MIR) reflectance spectroscopy

Quantification using infrared spectroscopy or gas chromatography are time-consuming and involves large amounts of environmentally harmful solvent waste. In contrast, visible near-infrared (vis-NIR) reflectance spectroscopy and mid-infrared (MIR) diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy offers a rapid and solvent-free alternative for the characterisation of TPH soil contamination (Forrester et al., 2013; Hauser et al., 2013).

The principle of NIR spectroscopy is based on the absorption of energy in the near infrared region (780 - 2500 nm) of the electromagnetic spectrum and advanced chemometrics or machine learning tools are required to extract useful quantitative and qualitative information. Multivariate calibration usually solves the problem of interference from compounds closely related to the analyte (Okparanma et al., 2014). In the NIR range the reflectance decreases with increasing contamination due to increased absorbance of contaminants (Douglas et al., 2017).

In the visible (vis) range (400 - 780 nm), absorption bands related to soil colour are due to electron excitations (Douglas et al. 2017). The vis-NIRS spectra can be affected by soil features such as moisture content, soil type and ambient lights (Douglas et al., 2017). Both techniques, vis-NIR and MIR, are now available as portable screening devices and can be deployed for in-field measurements without sample extraction. However, vis-NIR and MIR spectroscopy is not appropriate for the elucidation of chemical structures.

Earlier evidence demonstrated the applicability of vis-NIR sensor as a scanning technology for the rapid prediction of TPH contaminated soils (in the laboratory and onsite) as a solvent-free alternative for the characterisation of TPH in soil (Chakraborty et al., 2010; Okparanma et al., 2014). Later a new analytical approach combining vis-NIR with X-ray fluorescence spectrometry (XRF) was proposed for a rapid quantification of petroleum hydrocarbons in soil (Chakraborty et al., 2015). This technology is acknowledged as a fast and useful method in the evaluation of spatial variability of TPH, alkanes and PAHs in petroleum contaminated soils (Douglas et al., 2018). The authors combined Penalized Spline Regression (PSR) and Random Forest Regression (RFR) modelling approach and obtained a R^2 of 0.78 and RPD of 2.19 and concluded that this combined modelling methodology produced a better outcome compared to individual model-based analysis.

An accurate and alternative spectroscopic technique based on diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy does not require any sample preparation (e.g. soil extraction) prior to analysis. Thus, the neat soil sample can be studied directly simply by scanning the sample surface with the infrared beam and the reflected signal further analysed (Forrester et al., 2013). The investigation of multivariate models for the prediction of TPH concentrations in soil using DRIFT spectroscopy has been extensively investigated in the last decade (Chen and Tien 2020; Forrester et al., 2013; Nespeca et al., 2018; Ng et al., 2017; Webster et al., 2016).

Advantages	Limitations
• Does not require any sample extraction with solvents. • Fast detection of hydrocarbons. • Excellent accuracy (98%) for hydrocarbon analysis (MIR). • Reproducible. • Portable.	• Low performance of MIR spectroscopy mainly attributed to soil characteristics. • Instrument accuracy and reproducibility are affected by heterogeneous distribution of TPH, granulometric differences between soil types and particle aggregates. Therefore, sample preparation may be required to remove debris and homogenise the soil prior to measurement. • MIR is sensitive to variable moisture content, which contributes significantly to the non-linear response of instruments and low estimation accuracies. • Overlapping TPH absorption bands with those of naturally occurring in soil organic matter (SOM) in the MIR region, particularly those associated with the alkyl $-CH_2$ groups.

Imaging spectroscopy and remote sensing

Imaging spectroscopy (IS), or hyperspectral remote sensing, generates high spectral resolution optical images providing 98% accurate in discriminating petroleum contaminated soils (Correa Pabón et al., 2019; Gholizadeh et al., 2018). Petroleum hydrocarbons have no fundamental vibration, overtones, or combination modes in the long-wave infrared spectral region. Due to the lack of fundamental vibrations, the effect of petroleum hydrocarbons can be inferred through the investigation of changes in specific minerals that have observable spectral features in the long-wave infrared spectral region (Pelta and Ben-Dor, 2019). Imaging spectroscopy approach is a cost-effective method and particularly useful to detect small pipeline leaks before they become major spills (Correa Pabón et al., 2019), although the use is limited because the data is difficult to process (Schwartz et al., 2011).

Advantages	Limitations
• Particularly useful in detecting small pipeline leaks and the extend of the contamination. • Airborne sensors and hyperspectral remote sensing sensors with high spatial and spectral resolutions.	• Output data is difficult to process

Raman spectroscopy

In contrast to IR spectroscopy, where energy is absorbed, in Raman spectroscopy when a monochromatic light source interacts with the sample, photons can traverse, absorb, or scatter. Photon scattering can be elastic (Rayleigh) or inelastic (Raman), and this is used to assess the vibration of molecules such as PAHs. Because Raman scattering constitutes such a small fraction of the scattered light, it produces a relatively weak signal, therefore the source must be very intense and monochromatic, which invariably requires a laser. Thus, high safety requirements for laser operation are needed and OSHA safety standards for laser operation should be observed for safe operation.

A typical Raman spectroscopy system uses a laser capable of producing intense, monochromatic light to generate a “packet” of scattered light that can be collected, dispersed through a monochromator, and processed to produce a spectrum. Like infrared spectra, Raman spectra are unique to a given compound and hence can be used to “fingerprint” or uniquely identify as well as quantify chemicals on a surface, in a liquid, or in air.

Unlike infrared spectroscopy, the Raman signal is not affected by chemical species such as water, water vapour, and carbon dioxide. Fluorescent molecules that are often present in the environment can interfere with Raman spectroscopy. There are, however, methods that will overcome fluorescent interference while maintaining a strong Raman signal (US EPA, 2018).

Advantages	Limitations
• Quantitative measurement of multiple chemicals at one time. • The Raman signal is not affected by chemical species such as water, water vapour, and carbon dioxide.	• High detection limits in open path mode. • Presence of noise limits the detection limit of a particular compound. • Care is needed to avoid laser alteration of samples. • High safety requirements for laser operation. • High cost.

A1.2.4 Fluorescence

Ultraviolet fluorescence spectroscopy

Petroleum hydrocarbons can be detected with fluorescence techniques due to the presence of highly fluorescent components like polycyclic aromatic hydrocarbons and compounds with conjugated π bonds (Li et al., 2018). This technology is suitable for measuring the aromatic hydrocarbon portion of TPH independent of their carbon range. Aliphatic hydrocarbons do not fluoresce; thus, these cannot be detected by this technology.

In fluorescence spectroscopy, excitation of the molecules of the analyte by an ultraviolet (UV) light source leads to release of excess energy which then provides qualitative and quantitative information about the analyte. This phenomenon is described as fluorescence, when electrons within an atom when subjected to a light source absorb energy (excitation light) and alternate between energy states (i.e. from the fundamental state to excited states) – as the excited states are unstable, the electrons soon return to the ground state followed by the release of energy in the form of light in the UV range.

Sample preparation involves the extraction of petroleum hydrocarbons from soil using an organic solvent accordingly, the sample extract under analysis is placed in a quartz cuvette (plastic and glass absorb UV light) and further irradiated with UV light (USEPA, 2001b). A spectrum of fluorescence intensity versus emission wavelength is generated and detailed analysis of the spectrum allows the identification of known groups of hydrocarbons. The total concentration of the absorbing aromatic hydrocarbons is then determined from calibration curves generated with standards of known concentration and derived from the Beer-Lambert law, which gives the fluorescence intensity of an extract is directly proportional to the concentrations of aromatic hydrocarbons in the extract (USEPA, 2001b).

Some commonly used fluorescence spectroscopic methods include the SiteLAB® Analytical Test Kit UVF-3100A and the Rapid Optical Screening Tool (ROST®) laser-induced fluorescence (LIF) system. Although fluorescence methods do not determine aliphatic hydrocarbons, SiteLAB® Analytical Test Kit UVF-3100A software can estimate aliphatic hydrocarbon fractions and individual PAH or benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations, considering response factors based on aromatic and aliphatic hydrocarbon ratios obtained by off-site GC analysis (US EPA, 2001b). The Rapid Optical Screening Tool (ROST®) provides real-time subsurface (up to 150 feet below the surface) field screening of aromatic hydrocarbons (single, double and multi-ring) without any sample preparation (US EPA, 1997).

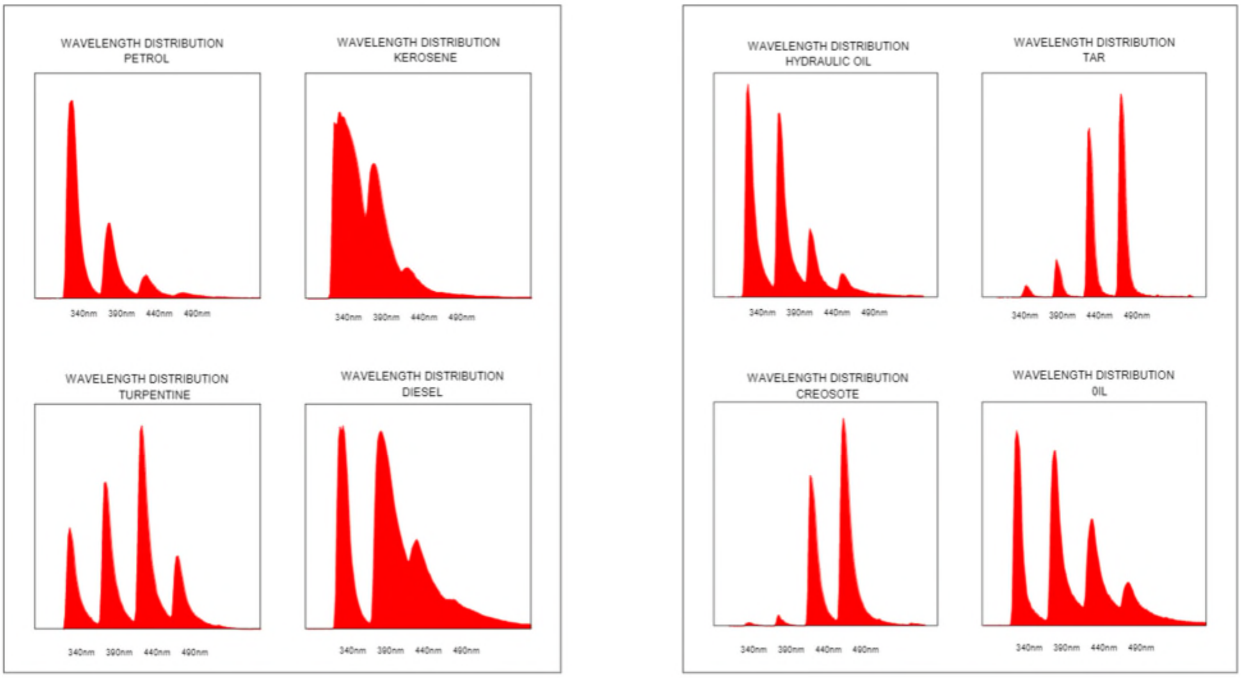
Advantages	Limitations
• Easy to use. • While training is necessary, personnel do not require high skills.	• Specificity to aromatic hydrocarbons. • Response factor must be developed to measure aliphatic hydrocarbons, and this cannot be done in the field but in the lab. • Fluorescence response is sensitive to soil matrix.

Laser-induced fluorescence

Laser-induced fluorescence (LIF) is a method for real-time, in situ field screening of residual and non-aqueous phase organic contaminants in undisturbed vadose, capillary fringe, and saturated subsurface soils and groundwater. The technology is intended to provide highly detailed, qualitative to semiquantitative information about the distribution of subsurface contamination that fluoresces, such as petroleum products containing polycyclic aromatic hydrocarbons (PAHs). An ultraviolet light-emitting diode (UV LED) can also detect monoaromatics (MAHs). Hydrophobic dyes that exhibit fluorescent characteristics can be injected into the subsurface ahead of the LIF probe window. These dyes partition into NAPL sources and emit a characteristic fluorescent pattern that is different from the unpartitioned dye, thus allowing for the detection of NAPL bodies. LIF sensors can be deployed on cone penetrometer (CPT) or percussion direct-push rigs. Note that if deployed on a CPT, soil behaviour-type data will also be collected, which can aid in the interpretation of site stratigraphy. Currently available LIF equipment is not designed to detect dissolved-phase contaminants.

LIF sensitivity to petroleum hydrocarbons on soil has been shown to be inversely proportional to the available surface area of the soil substrate. Sandy soils tend to have a much lower total available surface area than clay soils. A specific concentration of petroleum hydrocarbon compounds in sandy soils generally yields a correspondingly higher fluorescence response than an equivalent concentration in clay-rich soils (Bujewski and Rutherford, 1997). Typical waveforms fingerprints obtained with LIF systems for different oil types is shown in Figure A.1.

Figure A.1 Typical waveforms LIF fingerprints (Fugro).



A1.2.5 Colorimetry

Colorimetry is a technique by which the concentration of a compound in a coloured solution is typically measured using either a reflectance or absorbance colorimeter, or visually monitored using colorimetric test kits. Colour charts are provided in conjunction with colorimetric test kits and these are used for comparison with field results to determine the constituents and their approximate concentrations (US EPA, 2000b). A colorimeter is usually portable and works in the visible wavelength range (380 - 780 nm) of the electromagnetic spectrum operating at fixed wavelengths. A reflectance colorimeter measures the intensity of light reflected from solid particles in a reaction mixture, and an absorbance colorimeter measures the intensity of light that passes through the liquid portion of a reaction mixture. The working principle of the absorbance colorimeter/ spectrophotometer relies on the Beer-Lambert law (**Equation A**.1) that gives the light absorbed through an absorbing medium such as a solution, is directly proportional to the concentration of chemical species in solution. The law also assumes that there are no chemical changes in the sample. The cuvette that holds the solution is made either of glass or plastic (for visible radiation), is then inserted into the device and covered with an opaque light shield. A white visible light is emitted from the LED or tungsten lamp, focused, and passes through the solution. Part of the light is absorbed by the solution and the remaining is transmitted from the solution. Absorbance, which is defined as the logarithm of the ratio of the radiant power of the light source to that of the light that passes through the solution, is measured by a photoelectric detector in the device.

Equation A.1 Beer-Lambert law

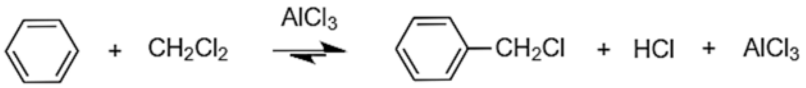
$$A = \log\left(\frac{I_0}{I}\right)$$

where A = Absorbance, I_0 = Intensity of light source and I = Intensity of light transmitted through the solution.

The TPH concentration is determined by plotting absorbance values for a series of reference standards of known concentration and the absorbance reading of the sample is then plotted on the calibration curve. However, some limitations of the use of a colorimeter include, the operation is restricted to only a few wavelengths; only coloured solutions can be analysed in colorimeters.

Colorimetric test kits provide qualitative or semi-quantitative screening of aromatic hydrocarbons in soil and water. The kits are designed for aromatic hydrocarbon analysis through the analysis of a coloured solution through the Friedel-Crafts alkylation reaction. An electrophilic aromatic substitution with an alkyl halide (e.g. dichloromethane, CH_2Cl_2) occurs to the aromatic hydrocarbon yielding the synthesis of alkylated products (polyalkylation may occur) in the presence of a catalyst, such as anhydrous aluminium chloride ($AlCl_3$) (Figure A.2). The coloured product absorbs light in the visible range of the electromagnetic spectrum. The aromatic hydrocarbon concentration in the reaction mixture is determined by comparing the intensity of the coloured solution with colour charts (EPA 2000b).

Figure A.2 Example of Friedel-Crafts alkylation reaction used in colorimetric test kits



This method is not dependent on analyte volatility, thus particularly useful for detection of older spills. Although, it may be difficult to detect TPH at low concentrations when comparing samples with the colour charts, taking into account that the detection limit is generally set within the range of 1 - 10 ppm. The extraction efficiency in clay soils is problematic. Additionally, the reaction products are sensitive to UV radiation and consequently there is the potential for overestimating the concentration, therefore, concentrations should be determined within 30 minutes of colour formation (US EPA, 2016). A spectrophotometer is designed to measure the amount of light absorbed or reflected by a specific compound. Colorimeters and UV/Vis spectrophotometers both measure sample absorbance to determine TPH concentrations. In contrast to colorimetry, UV-vis is more effective due to the use of a monochromator to select specific wavelengths to best detect the presence of specific compounds.

Advantages	Limitations
• Spectrophotometers are robust devices relatively easy to use • Low cost in terms of maintenance (i.e. lamp life cycle). • This method is not dependent on analyte volatility, thus particularly useful for detection of older spills.	• The extraction efficiency in clay soils is problematic. • Colours may be difficult to distinguish through visual inspection, particularly TPH at low concentrations. • Spectrophotometers used have low sensitivity to low sample concentrations, where concentrated samples are often required. • Potential for overestimation of concentrations should be determined within 30 minutes of colour formation. • In terms of selectivity, UV/Vis spectrophotometer do not discriminate compounds that absorb at the same wavelength. • The employed broadband detectors respond to all reflected light, thus having the potential to overestimate the sample concentration due to the effect of interferences or contaminants.

A1.2.6 Immunoassays/ bioassays

Immunoassay technologies are characterised by the use of biologically engineered antibodies to bind selectively with a target compound. The purpose of the assay is to identify and quantify these organic and inorganic compounds. Immunoassay technologies have been described as effective and inexpensive methods making their use preferable for on-site environmental analysis. The most commonly used immunoassay technique for TPH field testing is the enzyme-linked immunosorbent assay (ELISA) while other techniques such as fluorescence immunoassay (FIA) and electrochemical immunoassay (ECIA), and radioimmunoassay (RIA) have been also developed (see https://clu-in.org/characterization/technologies/immunoassay.cfm). In general, the immunoassay test kits are simple and quick to use, and these are often used for semi-quantitative screening of TPH in soil. They are best suited for the analysis of aromatic compounds (hydrocarbon fraction below C_7) and aliphatic hydrocarbons ($<C_{11}$). The determination of the target analytes concentration is achieved by comparing the colour developed by a sample of unknown concentration with the colour formed by the standard analyte of known concentration. The concentration of the analyte is estimated by visually comparing the colour intensity and compared to the colour/concentration values on a chart, or it can be measured more accurately with a photometer or spectrophotometer and the measurement compared to a reference value.

Enzyme-linked immunosorbent assay (ELISA)

ELISA is the immunoassay technique most often used for environmental field testing. ELISA offers high sample throughput, low detection limits, and it can be optimized for selectivity. This technique is preferable because it does not contain radioactive materials and is the simplest of all immunoassay methods. ELISA-based test kits are lightweight and more portable than the other methods. In ELISA, an enzyme conjugate binds to the antibodies, producing a colour. The generated colour is inversely proportional to the TPH concentration in the sample, i.e. the darker the colour, the lower the concentration. The final concentration can be determined by comparing the colour developed in the sample with that of a reference standard, either visually or by means of using a portable photometer or optical reflectance meter. Typical limitations include cross-reactivity in the presence of high PAHs concentrations, thus introducing false positives; immunoassay test kits are designed to detected specific analytes or a range of analytes, therefore a broad in-field screening is not likely; the operating working temperature range should be maintained at 4 - 32°C; and the test kits should not be used beyond the expiry date. Typical ELISA test kit is the RaPID® assays.

Advantages	Limitations
• High sample throughput. • Low detection limits. • Can be optimized for selectivity. • Does not contain radioactive materials. • Lightweight.	• Sample analysis by this method requires multiple steps. • Cross-reactivity in the presence of high PAHs concentrations. • The operating working temperature range (4 - 32°C) has a significant impact on detection limits. • Does not generate quantitative results, semi-quantitative only.

A1.2.7 Emulsion turbidimetry

Turbidimetry is a semi-quantitative screening method (output data drawn in the part-per-million (ppm) range) used in the assessment of petroleum hydrocarbon in soil. Turbidimetry shows relatively strong correlation with GC-FID results at a lower concentration range (0.01 - 0.1%) (Kong et al. 2017). The method is most sensitive to hydrocarbon compounds ranging from C_{12} to C_{30}, including diesel fuel and kerosene, with greatest sensitivity at the high end of the range (US

EPA, 2016). The operating principle is based on a methanol-based solvent extraction from hydrocarbons in soil. The concentration of TPH in soil is directly proportional to the amount of petroleum hydrocarbons present in solution.

A1.2.8 Fibre optical chemical sensors

While no handheld/or portable system analyser was identified as commercially available at the time of writing this report, fibre optic chemical sensors (FOCS) are often embedded with LIF systems. FOCS operate by transporting light by wavelength or intensity to provide information about analytes in the environment surrounding the sensor. The environment surrounding a FOCS is usually air or water. FOCS can be categorized as intrinsic or extrinsic.

Extrinsic FOCS simply use an optical fibre to transport light. An example is the laser induced fluorescence (LIF) cone penetrometer. The optical fibre is only a conduit for the laser induced fluorescence to be transported to an uphold detector. General extrinsic FOCS, such as the LIF, detect the presence of fluorescing hydrocarbons in the subsurface. Extrinsic FOCs can be chemical specific such as the laser-induced breakdown spectroscopy system (LIBS) is specific to monoaromatic and polycyclic aromatic hydrocarbons.

LIBS instruments are semi to fully quantitative, but generally they have ppm level detection limits. In contrast, intrinsic FOCS use the fibre directly as the detector. A portion of the optical fibre cladding is removed and replaced with a chemically selective layer. The sensor is then placed directly into the media to be analysed. Interaction of the analyte with the chemically selective layer creates a change in absorbance, reflectance, fluorescence, or light polarization. The optical change is then detected by measuring changes in the light characteristic carried by the optical fibre.

Intrinsic FOCS have been developed primarily to measure volatile petroleum constituents, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), and chlorinated volatile organic compounds (VOCs), such as TCE, PCE, and carbon tetrachloride, in water, air, or soil gas. Intrinsic FOCS are however not compound specific. Instead, they respond to classes of VOC or SVOC compounds.

Advantages	Limitations
• The design of FOCS provides in situ and real-time monitoring. • FOCS are small in size due to small fibre optic diameters. • Optical fibres are flexible within limits allowing greater access to difficult locations. • Transmission over long distances allows monitoring in deep wells and provides a measure of safety for monitoring hazardous atmospheres. • Multi-element analysis by intrinsic FOCS is possible using various fibres and a single central unit. • Portable Raman spectroscopy probes can be used to determine the concentration of PCBs in oil. • A LIBS probe mounted on a direct push platform can investigate heavy metal contamination at depth	• Many intrinsic FOCS are not compound-specific, react to many VOCs, and produce readings only for the concentration of total VOCs. The detection limits can be high compared with conventional analytical methods, such as gas chromatography. • FOCS are mainly used to detect gross contamination. • Some sensors are temperature and time dependent. A temperature sensor can be added to the probe containing the intrinsic FOCS to compensate for changes in temperature. Because sensor response is based on diffusion, the measured concentration may vary with the amount of time the intrinsic FOCS is in contact with the target analyte. Therefore, it is critical that equilibrium be achieved before a measurement is taken. Most intrinsic FOCS reach

Advantages	Limitations
	equilibrium in 5 to 10 minutes, which is indicated by a steady state signal. • The number of reversible reactions (adsorption and subsequent desorption), is limited, so intrinsic probes may have to be regenerated after extended use. • Because dynamic ranges are usually lower for intrinsic FOCs than for traditional electrodes, either the sample must be diluted, or the sensor recalibrated.

A1.3 DETAILS ON THE FIELD EQUIPMENT OR KITS FOR TPH ANALYSIS IN SOIL

A1.3.1 Field gas chromatography coupled to mass spectrometry systems

HAPSITE® INFICON® Inc.

Device description: HAPSITE® portable gas chromatograph-mass spectrometer (GC-MS) system manufactured by INFICON® Inc is a field-based analytical method as well as a laboratory instrument for measuring volatile organic compounds (VOCs) in water, soil and soil gas.

Operating procedure: The HAPSITE is designed to analyse VOCs in air, so samples must be introduced in the gas phase. In conjunction with a headspace equilibrium sampling accessory the instrument has the capability to analyse water and soil samples. The headspace analysis involves heating water or VOC contaminated soil (in water) in a closed sample container to a known temperature. Heat forces the volatile compounds to partition between the water and the space above the sample. After allowing sufficient time for equilibrium, the headspace containing VOCs from the sample is introduced to the HAPSITE as a gas sample. The HAPSITE portable GC-MS is capable of measuring VOCs with molecular weight typically 45 to 300 atomic mass unit (amu) range, boiling point approximately from -50 °C to +180 °C. (AMU is the measurable ion mass range of the mass spectrometer. A high upper value and wider range is a positive factor as it potentially allows identification of a wider range of analytes of interest). The internal standard gas is used as mass calibrator for compound identification and quantitation (California EPA Department, 2004).

Portable FLIR Griffin™ G510 GC-MS

Device description: The FLIR Griffin™ G510 GC-MS is a portable GC-MS equipped with an integrated injector allowing sampling of hazardous substances by injection of organic liquids. Liquid-extraction or solid-phase microextraction (SPME) is required, before introducing it to the injector on the GC-MS. In addition to a standard injector, the FLIR Griffin G510 is equipped with an air-sampling probe for vapour analysis. Using the air-sampling probe or injector port, detection of substances down to the ppb (parts per billion) level is possible.

Operating procedure: The 9-inch built-in touch screen provides automatic control and can be operated while wearing full PPE. The enclosure is IP65 is dust-tight, spray-resistant, allowing the use of FLIR Griffin™ G510 in adverse conditions. The system is equipped with a chromatographic column DB-5MS (15 m × 0.18 mm × 0.25 mm) programmable from 40 to 300°C and heating rate of 100°C/min, and a linear quadrupole mass analyser. The portable FLIR Griffin™ G510 GC-MS is provided with long-lasting batteries; built-in helium container connector (possible use of hydrogen is available); and the weight is 16.3 kg (including batteries, carrier gas and vacuum system). The system is calibrated with FC-43 (perfluorotrilamine); chemical identification is performed using the NIST library. Training requirements include 2 hours of basic work, 8 hours of operator certification.

Torion T-9 Portable GC/MS Perkin Elmer

Device description: The portable GC-MS Torion T-9 developed by Perkin Elmer offers rapid screening of chemicals, including environmental volatiles and semi-volatiles (VOCs/SVOCs), explosives, chemical warfare agents, hazardous substances, and for use in food safety and industrial applications. The integrated system features a low thermal mass capillary gas chromatograph with high-speed temperature programming and a miniaturized toroidal ion trap mass spectrometer (TMS) with a mass range from 41 to 500 Dalton. Samples are injected using a novel CUSTODION® solid phase microextraction (SPME) fibre syringe or a needle trap (CUSTODION-NT) (Elmer Perkin 2020). The system is equipped with an MXT-5, 5 m × 0.1 mm × 0.4 µm df GC column, adjustable between 40 to 300°C (up to 2.5°C/sec or 150°C/min).

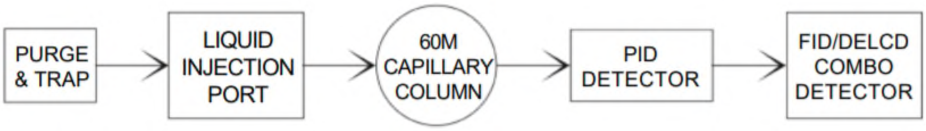
Operating procedure: The top panel of the Torion T-9 GC-MS contains the battery compartment, display screen, power and operating buttons, SPME sample injection port, memory card slot, Ethernet port, carrier gas cartridge connection, status lights, and manual shut-off access. The internal components are precision mechanical and electronic parts, including heaters, vacuum pumps, pressure controller, gas flow lines, circuit boards, CPU, SPME injector, low thermal mass GC, and TMS.

Environmental and BTEX GC Systems SRI INSTRUMENTS

Device description: The system Environmental and BTEX GC Systems developed by SRI INSTRUMENTS is a field GC equipped with a PID and FID/DELCD detectors and includes a built-in EPA Method 5030 or 5030/5035 compliant Purge & Trap for concentration of liquid and/or soil samples. Also, the standard on-column injection port allows for direct syringe (liquid) injection, and a second injector may be installed if desired. A 60 m capillary column (customized) is installed in the system and programmable column oven up to 400 ¤C. The BTEX/Environmental GC systems can analyse gas, water, and soil samples. Detection limits for PID - ppb range/ Purge & trap – down to ppt range.

Operating procedure: To detect commonly targeted pollutants, the Environmental GC uses a sensitive, non-destructive PID detector in series with a combination FID/DELCD detector. The PID detector responds to compounds whose ionization potential is below 10.6 eV, including aromatics and chlorinated molecules with double carbon bonds. The FID detector responds to the hydrocarbons in the sample. The DELCD selectively detects the chlorinated and brominated compounds in the FID exhaust (Figure A.3). Since the sample is pre-combusted in the FID flame, the DELCD is protected from contamination due to hydrocarbon overload. An advantage of using detectors in series, peaks on the FID chromatogram that are obscured by the methanol peak are visible on the PID chromatogram (Instruments SRI, 2020b).

Figure A.3 Theory of operation of Environmental GC System (Instruments SRI, 2020b)



The BTEX GC is the same as the Environmental GC without the DELCD detector. Both systems have a "whisper quiet" internal air compressor and can be used with an H_2 -50 hydrogen generator for tankless field operation. The BTEX/Environmental GC systems can analyse gas, water, and soil samples. Four types of injection techniques can be used: purge and trap, direct liquid injection, TO-14 type gas sample concentration, and manual headspace injection. The

Purge & Trap concentrator may be used for gas, liquid, and solid samples. For liquid samples up to 5 µL and gas samples up to 1 mL, direct injections can be made through the on-column liquid injection port. Larger gas samples can be injected through the syringe port on the 5030/5035 Purge & Trap concentrator or the septum port on the 5030 model (Instruments SRI, 2020b).

FROG-5000™ Portable GC

Device description: The Frog-5000 portable gas chromatograph (GC) manufactured by Defiant Technologies identifies multiple target volatile organic compounds (VOC) in water, soil, and air from low ppb levels. The measuring range extends from vinyl chloride (MW 62.5) to 2-methylnaphthalene (MW 142.2). Qualitative and quantitative analysis is obtained within 10 minutes. The detection is accomplished by the use of an internal Photoionization Detector (PID). The FROG-5000 is not recommended for analysis of diesel due to inconsistent results. First there is the issue of solubility, diesel is not soluble in methanol which is the solvent of choice for preparing standards to be used with the Frog. This inconsistency is best explained by the inefficiency of sparging of diesel samples. If a calibration is attempted one will find that there is no correlation between peak area and concentration.

Operating procedure: The Frog-5000 portable GC system is equipped with a MEMS (micro electro-mechanical systems) and has an integrated heater for temperature ramp chromatography; featuring a 5.2 m GC column; and combined with an internal PID for the identification of VOCs in ambient air at concentrations as low as 1 part per billion. Purification steps with mol sieves and activated charcoal are used both at the introduction of samples and analysis.

Specifications include: 9 hours battery lifetime (lithium-ion batteries); dimensions 11 x 7.75 x 12 inches; weight 2.1 kg; GC column 5.2 m; PID lamp 10.6 eV; interface standard RS-232 port; microSD card enables data transfer; Ellvin™ chromatography software.

A1.3.2 Field detectors

MicroFID II Portable Flame Ionization Detector

Device description: The MicroFID II Portable Flame Ionization Detector developed by Photovac and commercially available from Environmental Monitoring features fuel capacity 10 L; fuel life 10 hrs; battery life 15 hrs, datalogging 24,000 interval mode; response T90 <3 secs; range 0 - 50,000 ppm (5%); resolution 0.1 ppm; repeatability ± 2%; weight 6 kg. The unit has a metal hydride gas canister (compact "pencil" canister) avoiding hazardous transportation, a datalogging system using remote ATEX-certified Bluetooth data acquisition with GPS datalogger. The MicroFID II has a measuring range of up to 50,000 ppm concentration (5%).

Operating procedure: An FID uses a flame to ionize organic compounds containing carbon. Following separation of the sample in the GC column, each analyte passes through a flame, fuelled by hydrogen and zero air, which ionises the carbon atom. Once formed, the ions are collected and measured as they create a current at the detector's electrodes. The current is produced as the detector collects the charged ions. The current is then converted to an electrical signal in picoamperes (pA) or millivolts (mV). Reader is referred to the DataFID Operating manual for further information available at https://www.em-monitors.co.uk/products/vocs-fid-pid/.

MiniRAE and RKI Eagle 2

Device description: The handheld photoionization detector (PID) such as MiniRAE and RKI Eagle 2 can detect VOCs (aromatic and chlorinated) and petroleum constituents including benzene, toluene, ethylbenzene and xylene (BTEX) in the headspace above a soil sample (ppm levels). The PID is a non-destructive detector that can be used in series before other detectors. Using multiple detectors extends the range of compounds that can be detected in one analysis. PID is sensitive to humidity and may require frequent recalibration.

Operating procedure: A PID consists of an ultraviolet lamp, ranging in energy from 9.5 to 11.7 eV, mounted on a low-volume flow-through cell. As constituents of the sample pass through the cell, they are energized and ionized. The ions are collected at positively charged electrodes, where the change in current is measured. The current produced is proportional to the gas concentration of organic molecules. A 10.6 eV lamp is typically used for petroleum hydrocarbons, as it will not ionize methane and some chlorinated hydrocarbons with higher ionizing potential. A few halogenated compounds that have ionization potentials of less than 11.7 eV can be detected by the higher-energy PID. The PID is more selective than the FID. MiniRAE and RKI Eagle 2 are battery operated; MiniRAE provides 16 hours of operation period (12 hours with alkaline battery), while RKI Eagle 2 provides 18 hours (alkaline battery). Both MiniRAE and RKI Eagle 2 output signal is referenced to isobutylene.

A1.3.3. Field spectrometers

Infracal® TOG/TPH Analyser

Device description: Infracal® analyser manufactured by Wilks Enterprise, is a quantitative field measurement technology based on optical IR analysis, suitable for measuring aromatic and aliphatic hydrocarbons independent of their carbon range. Infrared spectroscopy is useful for measuring the TPH of hydrocarbons in the C_6 to C_{26} range, however, results are biased toward hydrocarbons greater than C_{12} because of their greater response to IR, and because larger hydrocarbons volatilize less during extraction (US EPA 2001c). Infrared analysis using the Infracal® TOG/TPH Analyser involves use of a single-beam, fixed-wavelength, nondispersive infrared (NDIR) spectrophotometer to determine the concentration of petroleum hydrocarbons in a liquid sample extract.

Operating procedure: During infrared analysis using Model CVH, a sample extract is placed in a quartz cuvette that is then inserted into the spectrophotometer. A beam of infrared light is then passed through the sample extract. Infrared sources are generally continuum sources, which emit radiation at intensities that vary smoothly over ranges of wavelengths. The average sample extraction and analysis time for Models CVH and HATR-T is 10 to 20 minutes per sample. Model HATR-T featured a method detection limit of 76 mg/kg (diesel soil) and linear range of 1 – 5000 ppm (US EPA 2001c). For both Models CVH and HATR-T, the TPH concentration in a sample extract can be determined by comparing the absorbance reading to a calibration curve of absorbance values and corresponding hydrocarbon concentrations for a series of known standards selected based on the type of PHCs being measured at a site. The Infracal® TOG/TPH Analyser presents results in units selected by the user during calibration, such as mg/kg in soil, mg/L in liquid, or absorbance values. The device displays results as mg/kg in soil by default. The Infracal® TOG/TPH Analyser has a standard, nine-pin, female DB9 connector (RS232-C) for serial data communication. The manufacturer offers an optional software package, InfraWin, that allows the user to connect a personal computer to the device and automatically download, label, and save measurement results; remotely control measurement parameters; generate and store multiple calibration tables; and report measurement results in various numerical and graphical formats (US EPA 2001c). The device can be rented on a monthly basis for 15% of the purchase price; as a result, the breakeven point between the purchase price and the rental cost is about 7 months. The InfraCal 2, the latest introduction to the analysers, uses the same measurement technology as the InfraCal TOG/TPH analysers with added features such as data storage and transfer, multiple calibrations and password protection for instrument settings (Spectro Scientific, 2020).

ASD FieldSpec 4 portable spectroradiometer

Device description: The full-range (350 - 2500 nm) Vis-NIR FieldSpec 4 Hi-Res (ASD Malvern Panalytical) provides high resolution for very accurate contact reflectance measurements and available in a portable, ruggedized spectroradiometer. The enhanced spectral resolution is particularly useful for detecting and identifying compounds with narrow spectral features in the longer wavelengths such as alteration mineralogy and gases for atmospheric analysis.

Operating procedure: Dimensions 12.7 x 36.8 x 29.2 cm; weight 5.44 kg; resolution 3 nm (700 nm) and 8 nm (1400/2100 nm); scanning time 100 milliseconds; operating temperature 0 to 40°C; wavelength accuracy 0.5 nm. Communications via 10/100 base T Ethernet port with ethernet cross-over cable and wireless; battery operated (approximately 6 hours); NIST traceable calibration; software RS3™ spectral acquisition software, Seamless interface with ENVI®, ASD ViewSpec™ Pro for post processing Optional Indico™ Pro.

RemScan® handheld mid-infrared instrument

Device description: The RemScan® technology developed by Ziltek, uses a diffuse reflectance mid-infrared (MIR) Fourier transform (DRIFT) spectrometer for accurately estimate TPH concentration expressed in mg/kg for compounds ranging from C_{10} to C_{36} (Khudur and Ball 2018). The instrument demonstrated a particularly good accuracy below 5000 mg/kg, according to the manufacturer's figures. Recent evidence showed considerably greater variation for TPH content less than 8000 mg/kg and for heavily contaminated soil samples (>100,000 mg/kg), therefore conventional GC analysis is recommended for validation of higher concentrations (Chen and Tien 2020). The instrument detection limit was of 208 mg/kg according to a previous study (Chen and Tien 2020) although detection limit typically 68 mg/kg TPH is indicated by the manufacturer (Ziltek 2020). The impact of different soil types and TPH concentrations detected in the calibration models were thoroughly evaluated recently (Chen and Tien 2020; Ng et al. 2017; Webster et al., 2016). The performance of the MIR spectrometer was recently evaluated for the prediction of TPH in three different diesel-contaminated soils types including, a carbonate dominated clay, a kaolinite dominated clay and a loam from Padova (Italy), north Western Australia and southern Nigeria, respectively, (Webster et al., 2016) and the response validated against standard laboratory analytical methods (Chen and Tien, 2020; Khudur and Ball, 2018; Webster et al., 2016). Particular attention must be paid to the fact that all samples were air-dried (soil moisture < 5%) before scanning, since spectroscopic techniques such as MIR, are known to be sensitive to variable moisture content. For high moisture applications, Ziltek can provide a Portable Drying Unit. The unit dries batches of up to 35 soil samples in 30-60 minutes. The MIR output data significantly correlated to TPH concentrations by GC-MS and associated errors were attributed to soil organic matter content and soil texture, where clay and silty clay soils were predominantly not detected by the MIR spectrometer (Chen and Tien, 2020; Ng et al., 2017). The authors suggested that the calibration of various types of soil textures may increase the applicability of the MIR technique prior to field screening. Recent evidence showed that the weathering effect in diesel-contaminated soil did not impact significantly on the detection accuracy of the MIR spectrometer (Chen and Tien, 2020).

Operating procedure:

- The sample is placed in the "Sample Cup" provided, mixed thoroughly using a spatula and then tamped using the "Sample tamper".
- Due to the soil heterogeneity, the same soil sample needs to be scanned 5 times with mixing in between scans and then average the 5 readings.
- The soil needs to be air-dried as the moisture may affect the accuracy of TPH concentration reading. A portable drying unit is available to purchase from Ziltek.
- RemScan® can detect moisture in the soil where a warning message is displayed on the PDA (personal digital assistant) or the tablet.

- RemScan® transfers the signal to concentration (mg/Kg) and displays it on the PDA or the Tablet that comes with the updated models.
- Battery life – 8 hours for PDA and 4 hours per battery for instrument (comes with 3 batteries) for full day field usage.

Agilent 4300 Handheld FTIR

Device description: The non-destructive handheld Fourier Transformed Infrared (FTIR) (mid-infrared) spectrometer manufactured by Agilent Technologies, is ideal for rapidly mapping the surface of materials for the prediction of TPH, including aliphatic (alkanes) and polycyclic aromatic hydrocarbons (PAH) (Douglas et al. 2019a; Wang et al. 2019; Wang et al. 2020). The instrument is suitable for resolving dominant hydrocarbon fractions (C_n) in soil, however, is not able to determine each alkane in heterogenous mixtures. The linear range for petroleum hydrocarbon measurements was determined from 0.5 to 50 g/kg (Wang et al. 2020). Calibration with single alkane standards provided evidence that concentrations were accurately estimated, and these were applied using the bands at the specific IR region after baseline correction (Wang et al. 2019). The total concentration of the alkane mixture can be determined using absorbance area of a region below 3000 to 2800 cm^{-1}. It has been reported that the shorter carbon chain fractions C_{20} and C_{26}, and longer carbon chain C_{32} and C_{37} can be identified using the intensity ratios (Wang et al. 2019).

Operating procedure: Real-time analysis mode and rapid scan rate (measurements take less than 20 seconds) make it easy to analyse the surface of an object, determine areas for more in-depth measurements, and develop a “molecular map” of the object’s surface. The touch-screen user interface is intuitive and runs the MicroLab Mobile software. The handheld detector is equipped with hot swappable 4-hour lithium ion batteries and the system is GLP/GMP compliant. The MIR spectroscopic technique is known to be sensitive to moisture content, thus, the performance of the handheld FTIR was similarly tested in order to investigate the prediction of TPH, including alkanes and PAHs in field-moist contaminated soil samples from Niger Delta, Nigeria and further validated against GC-MS analysis (Douglas et al., 2019 a). The instrument is equipped with a deuterated triglycine sulfate (DTGS) thermal detector and a zinc selenide beam splitter, providing a linear response independent of wavelength. The collected raw spectra in reflectance (R) are firstly converted into reflectance (log(1/R)) followed by noise reduction, normalization and baseline corrections prior to modelling. The enhanced models performance accuracy of the field-portable Agilent 4300 to predict TPH concentrations (RSME = 1592 mg kg^{-1} and $R^2 = 0.89$) (Douglas et al., 2019a) was reported to be better than those obtained using the handheld RemScan® mid-infrared spectrometer (Webster et al., 2016). Similarly, greater accuracy for TPH detection using MIR (Agilent 4300) over that of vis-NIR was reported for the same batch of samples (Douglas et al., 2018).

QualitySpec Trek spectrometer

Device description: The handheld QualitySpec Trek is a portable full-range vis-NIR spectrometer manufactured by ASD Inc., Longmont, CO, USA and measures the almost bidirectional reflectance of NIR and SWIR radiation at 350 - 2500 nm wavelengths with a spectral resolution of 9.8 nm at 1400 nm.

Operating procedure: The instrument has three detectors: 350 - 2500 nm (512-element silicon array), 1001 - 1785 nm (InGaAs photodiode), and 1786 - 2500 nm (InGaAs photodiode). The instrument also has an internal light source and internal gray scale reference for optimization and wavelength calibration. The light source is a Quartz Tungsten Halogen bulb with a colour temperature of 2870 ± 33 K. The resulting reflectance is absolute reflectance (reflectance normalized with reference reflectance) (Leppänen and Kontu, 2018). The instrument includes an integrated internal light source, on-board GPS, voice audio recorder for expanded sample descriptions, internal white reference for hands-free optimization and calibration, lightweight rechargeable lithium ion batteries, internal wavelength reference, integrated computer and LCD display with easy push button navigation and a PC-based project and data management software ecosystem.

Horiba OCMA-350 Oil Content Analyser

Device description: Horiba infrared (IR) spectrometer targets mid- to high range hydrocarbons (C_{10}-C_{36}), depends on calibration standard, with greater response to aliphatic hydrocarbons. The spectrometer has a MDL of 1 mg/kg and measuring range 0 to 1000 mg/kg for oil in soil (US EPA, 2001d).
Operating procedure: The OCMA-350 uses the highly effective, environmentally safe S-316 extraction solvent to extract the oil components from oily water samples, soil samples, or product surfaces. The extract is analysed using IR absorbance, measuring absorption in the 3.4 to 3.5 μm range. HORIBA's S-316 Solvent can be recycled with the aid of the optional SR-300 Solvent Reclaimer. The extracted solution is placed into the measuring quartz cell (20 mm cell length) and set in place (Horiba, 2020).

A1.3.4. Field fluorescence systems

Five laser-based induced-fluorescence systems and one light-emitting diode system (UV LED) are currently available including:

1. Rapid Optical Screening Tool (ROST®) System
2. Site Characterization and Analysis Penetrometer System (SCAPS) LIF Sensor and Support System
3. Tar-Specific Green Optical Screening Tool (TarGOST®)
4. UltraViolet Optical Screening Tool (UVOST®)
5. Dye-Enhanced Laser Induced Fluorescence System (DyeLIF™)
6. Ultraviolet Light Emitting Diode (UV LED)

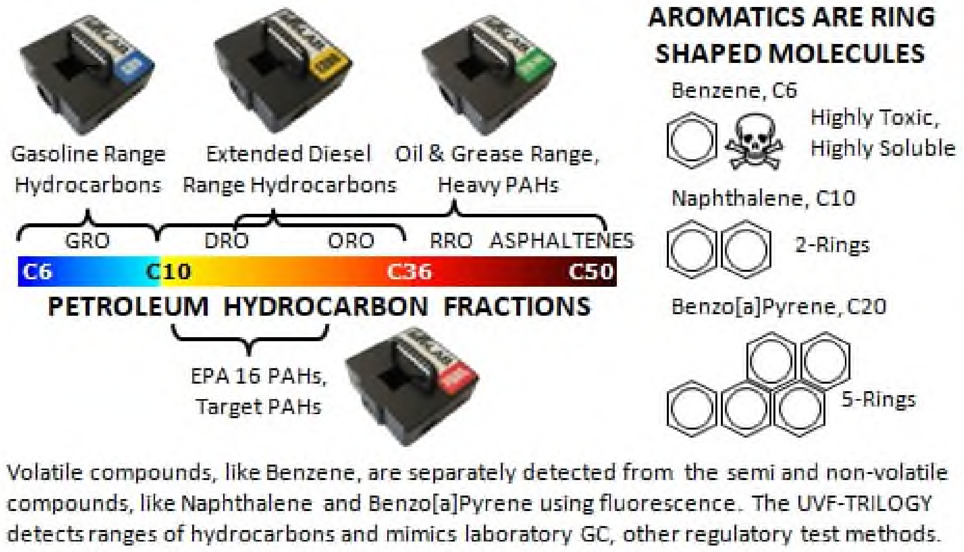
The first five UV fluorescent systems currently commercially available use a technology developed wholly or in part by Dakota Technologies. They differ primarily in the laser used to excite the PAHs. The captured fluorescent light of each PAH mixture presents a distinctive wavelength/time matrix (WTM). The WTM, however, cannot be produced while the probe is moving. By sampling the total fluorescence at different wavelength channels and optically delaying the fluorescence pulses to photomultiplier tubes that are recorded with an oscilloscope, a multi-wavelength waveform is created. The waveform allows the simultaneous observation of the spectral and temporal qualities of the fluorescence with depth and can be used to identify different products. The sixth available system is the Fuel Fluorescence Detector (UV LED), which uses an LED rather than a laser to generate UV light at 254 nm. Fluorescent light from MAHs and PAHs is captured downhole by two photomultiplier tubes. The dual photomultipliers allow qualitative differentiation between light and heavy fuels.

Analytical Test Kit UVF-3100A

Device description: The UVF-3100A is a quantitative field analyser developed by SiteLAB® Corporation for TPH analysis in soil samples, gasoline, jet fuel, diesel fuel, heating oils, crude oils, lube oils, creosote, coal tars and many other types of petroleum hydrocarbons. The system is based on ultraviolet fluorescence spectroscopy and provides results in soil, sediment or water samples with solvent extraction and detection limits are dependent on calibration kit used: Gasoline Range Organic Hydrocarbons (GRO) = 0.5 ppm, Extended Diesel Range Organic Hydrocarbons (EDRO) = 0.1 ppm, Polycyclic Aromatic hydrocarbons (PAH) = 0.05 ppm and TPH-Oil = 0.5 ppm. The system has specificity to aromatic hydrocarbons which emit energy at specific wavelengths (SiteLAB, 2020b). The fluorometer's response of each sample is measured by the instrument on a linear, multi-point calibration curve using certified standards sensitive to the wavelengths of interest. Samples are extracted and concentration measured in solvent using disposable test kits. The concentration is displayed in ppm or ppb or raw fluorescence, in only a few seconds. Each sample takes about 5 to 10 minutes to process; analysis time is 5 to 10 seconds (SiteLAB, 2020a).

The UVF-TRILOGY was designed to mimic the GC methods, which can separate TPH into gasoline range, diesel and oil range hydrocarbon fractions. Therefore, different UV modules (Figure A.4) are commercially available to best fit the source spill. SiteLAB provides a variety of different calibration kits to choose from in order to best match the source of the spill and provide maximum performance when comparing field results to the confirmatory lab (SiteLAB, 2020a).

Figure A.4 UVF-3100A field analyser and different UV modules available (SiteLAB, 2020a).



The operating temperature range for the UVF-3100A is 7 to 36°C. The lowest operating temperature is based on the possibility of the fluorometer's quartz crystal display freezing. According to SiteLAB, the UVF-3100A does not have a storage temperature or operating humidity restriction. The UVF-3100A Extraction System has a purchase price of $11,999. SiteLAB also rents the UVF-3100A at a rate of $500 per day which includes calibrated analyser, field case, and all tools needed to prepare samples for analysis. Specify which UV module is required or combo of two, and purchase of sample extraction kit as needed. The system requires external power supply, 100-240 VAC, Max. 30 watts. The system is approved by CE, UL and C-UL. ISO 9001 manufacturing (SiteLAB 2020 b).

Connecting the UVF-3100A to a computer allows downloading and manipulation of calibration and sample data using SiteLAB software, although a computer connection is not needed to collect or read data. To connect the device to a computer, an RS-232 cable connection is used.

Operating procedure: Measuring TPH in soil using the UVF-3100A involves the following two steps: (1) extraction and (2) concentration measurement. The UVF-3100A can measure both GRO and EDRO components of sample extracts. Both analyses may be performed on one sample extract; however, the emission filter must be replaced and the device must be recalibrated between the GRO and EDRO analyses (US EPA, 2000b).

Step 1 - Extraction

1. Measure 10 g of soil sample and place the measured amount in a high-density polypropylene sample extraction jar.
2. Add two steel mixing balls to the jar. For clay soil, add three mixing balls to the jar.
3. Add 10 mL of methanol to the jar and cap the jar.
4. Manually shake the jar for 2 minutes. If multiple jars must be shaken, use the shaker/mixer can, which can hold up to five jars.
5. If soil particles are visible in the jar, allow the soil to settle for 1 to 2 minutes.
6. Use a syringe with a detachable filter to transfer 3 mL of filtered extract into a test tube.
7. Cap the test tube, and let it stand until concentration measurement is performed.

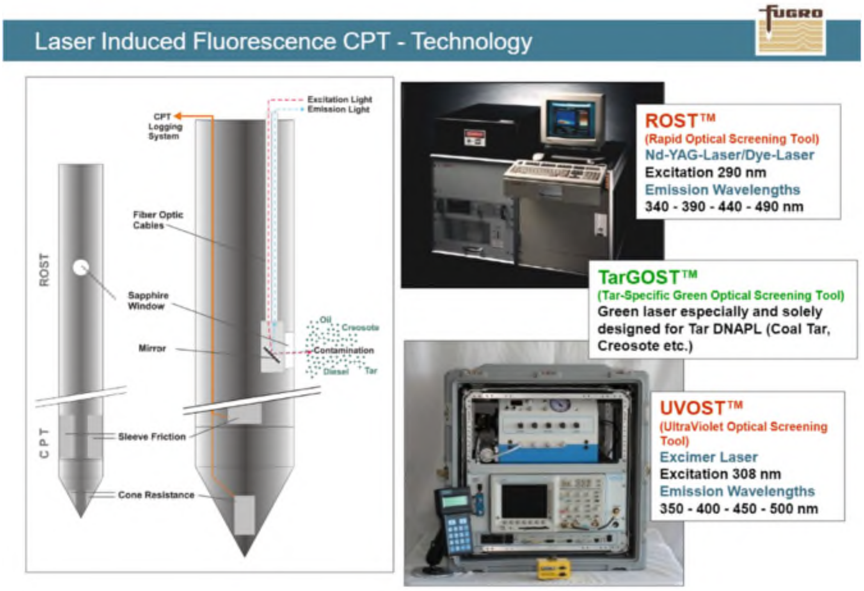
Step 2 - Concentration Measurement

1. Decant the extract from the test tube into a quartz cuvette. Place the cuvette in the sample chamber of the UVF-3100A.
2. The device displays concentrations in ng/L, µg/L, mg/L, parts per trillion, parts per billion (ppb), ppm, or fluorescence units. Device readings may be downloaded to a computer and compiled with other data as part of a spreadsheet or may be manually recorded from the UVF-3100A display.
3. The concentration measured represents only the aromatic hydrocarbons present in the sample extract. The aliphatic hydrocarbon concentration may be estimated using the UVF-3100A software.

Rapid Optical Screening Tool (ROST®) System

Device description: The Rapid Optical Screening Tool (ROST®) System (Figure A.5) is licensed to Fugro Geosciences and consists in a tuneable dye LIF system designed as a field screening tool for detecting aromatic petroleum hydrocarbons in the subsurface of soils (up to 45 m below the soil). It uses a dye laser (280 nm to about 300 nm) mounted in a CPT rig. ROST® LIFs can detect most fuels and oils. They generally do poorly with heavier hydrocarbon mixtures such as coal tars, creosote (unless cut with diesel), and bunker C. ROST system does not detect monoaromatics, polychlorinated biphenyls, chlorinated alkenes and alkanes, or explosives. The ROST system permits temporary or permanent installation of the LIF equipment on a CPT truck or other direct push vehicle, although a dedicated ROST unit could be permanently installed in a CPT.

Figure A.5 Overview of LIF CPT technology (Fugro)


Laser Induced Fluorescence CPT - Technology

ROST™
(Rapid Optical Screening Tool)
Nd-YAG-Laser/Dye-Laser
Excitation 290 nm
Emission Wavelengths
340 - 390 - 440 - 490 nm

TarGOST™
(Tar-Specific Green Optical Screening Tool)
Green laser especially and solely designed for Tar DNAPL (Coal Tar, Creosote etc.)

UVOST™
(UltraViolet Optical Screening Tool)
Excimer Laser
Excitation 308 nm
Emission Wavelengths
350 - 400 - 450 - 500 nm

Operating procedure: The spectrometer rack holds all the spectroscopic instrumentation, including the Nd:YAG pump laser, tuneable dye laser, emission monochromator, photomultiplier tube, and associated power supplies and motion controllers. The control rack contains the control computer and a digital oscilloscope signal processor. In operation the racks can be positioned independently and separated from each other by up to 7.6 m. The racks themselves are standard industrial models with a 0.5 by 0.6 m footprint and stand 0.63 m high.

The Nd:YAG pump laser and dye laser are arranged on an optical breadboard affixed to the top of the spectrometer rack. When the opaque plastic dye laser cover is in place, the total height of the spectrometer rack is 0.86 m. The computer monitor can be conveniently placed on top of either the control rack or the dye laser cover. The system has a linear response up to 10,000 mg/kg. In sandy soils, the non-linearity occurs at lower concentrations than in clay rich soils, possibly due to self-absorption or saturation. LIF sensitivity to petroleum hydrocarbons in soil has been shown to be inversely proportional to the available surface area, i.e. sandy soils have a much lower surface area than high clay content soils (US EPA, 1997).

Site Characterization and Analysis Penetrometer System (SCAPS) LIF Sensor and Support System

Device description: The Site Characterization and Analysis Penetrometer System (SCAPS) was one of the first systems to deploy a LIF probe. SCAPS is a rapid in-field soil and groundwater analysis system that provides cost-effective characterisation of soil conditions to depths of up to 30 m or more. SCAPS uses a truck-mounted cone penetrometer system to directly push an instrumented probe into the ground for rapidly characterising soil types and detecting and delineating the presence and extent of subsurface contamination. A variety of sensors can be attached to the probe to detect different compounds. LIF sensors are typically used to detect petroleum compounds.

Several different types of sensors and sampling tools mounted on the SCAPS have been tested. The thermal desorption and Hydrosparge sensors/samplers are used to detect VOC in soil and groundwater. The thermal desorption sensor/sampler consists of a nose cone with a sampling chamber that can be opened to collect a soil sample. The sample is heated to volatilise the VOCs. The vapours are then transported to the surface, where they are analysed by a portable mass spectrometer. The Hydrosparge sensor/sampler inserts a sparge into a groundwater boring formed by the cone penetrometer. Using helium gas, it then purges the VOCs from the water, and transports them to the surface, where they are also analysed by a portable mass spectrometer.

Operating procedure: The SCAPS LIF system uses a pulsed laser coupled with an optical detector to measure fluorescence via optical fibres. The CPT LIF systems use a steel probe containing the LIF sapphire optical window and cone, and sleeve strain gauges. The SCAPS LIF system detects aromatic hydrocarbons that fluoresce when excited at 337 nm (US EPA, 1997 b). This wavelength will excite aromatic compounds with three or more aromatic rings as well as some two-ring compounds.

Tar-Specific Green Optical Screening Tool (TarGOST®)

Device description: TarGOST® was designed specifically for detecting coal tars, creosotes, and other heavy oils. It is a Dakota Technologies tool that can be used with CPT or percussion-driven equipment.

Operating procedure: The TarGOST® system uses an Nd:YAG laser emitting at a green visible light frequency of 532 nm. The TarGOST® measures wavelengths at 532, 570, 620, and 670 nm. The waveform response areas are calculated and presented as a percent of RE value. These values are displayed in graphical form as a function of depth or fluorescence versus depth log (CLU-IN 2020a).

UltraViolet Optical Screening Tool (UVOST®)

Device description: The UVOST® system developed by Dakota Technologies, readily detects light to mid-weight fuels and oils containing two to four aromatic rings PAHs, i.e. gasoline (highly weathered and/or aviation gas yield is very low to zero), diesel, jet (kerosene), motor oils, cutting fluids, hydraulic fluid, light crude oils, and fuel oils. The UVOST® system has a typical detection limit of 10-500 ppm (NAPL type and soil dependent).

Operating procedure: The UVOST® system can be deployed on CPT or direct-push rigs and is available from a number of vendors. The UVOST® system uses an XeCl excimer laser to generate very fast pulses of 308 nm UV light at 50 Hz. The light is transmitted via fibre optics to a sapphire optical window that illuminates the adjacent soil. Both reflected transmission light (scatter) and any fluorescence is reflected by mirror and sent to a monochromator at the surface. A cut-off long-pass filter is placed at the front of the monochromator to reject the vast majority of emission laser light but pass the lower energy (longer wavelength) fluorescence (CLU-IN, 2020).

Dye-Enhanced Laser Induced Fluorescence System (DyeLIF™)

Device description: DyeLIF™ (Dakota Technologies) was designed specifically for detecting chlorinated solvent DNAPL. This tool that can be used with CPT or percussion-driven equipment.

Operating procedure: Because chlorinated solvents do not generally contain components that fluoresce, the DyeLIF™ system introduces an aqueous delivery fluid containing a hydrophobic dye through a small injection port that is situated 22 cm below the LIF window. When DNAPL is present, the dye will partition into it in less than one second. The fluorescent response of the solvated dye is much more intense and is distinct from that of the unsolvated dye. The response is monotonic; more fluorescence equates to higher pore saturation of DNAPL. The waveform response areas are calculated and presented as a percent of RE value. These values are displayed in graphical form as a function of depth or fluorescence versus depth log (CLU-IN, 2020).

Ultraviolet Light Emitting Diode (UV LED)

Device description: The UV LED system made by Vertek Manufacturing. The system uses a metal housing with a sapphire optical window that is mounted above the cone and sleeve strain gauges of a CPT rig (CLU-IN, 2020).

Operating procedure: The UV LED is most successful at detecting jet fuel, diesel, gasoline, monoaromatic releases (benzene, toluene, ethylbenzene, and xylenes), and home heating and motor oil. It is unlikely to detect coal tars, creosotes, penta-chlorophenols, or bunker C. It does not detect polychlorinated biphenyls, chlorinated alkenes and alkanes, or explosives. Detection limits are in the 100 to 500 ppm range, depending upon soil and petroleum type.

A1.3.5. Colorimetric field kits

Hanby TPH soil kit

Device description: Hanby TPH Soil Kit is a colorimetric test kit developed by Hanby Environmental and provides qualitative and semi-quantitative analyses in less than 5 minutes for petroleum substances in soil and water samples. The test kit provides results for petroleum fuels and constituents, such as gasoline, diesel fuel, jet fuel, crude oil, motor oil, BTEX, and PAHs, as well as PCBs in soil and water samples. The typical range of the test is 1.0 to 1,000 mg/kg and typically achieves detection limits of 1.0 mg/kg in soil.

The Hanby test specifically responds to aromatic compounds found in fuels and polychlorinated biphenyls (PCB). The test is based on the Friedel-Crafts reaction, in which electrophilic aromatic substitution produces molecules with intense colouring. The Hanby field test kit comes in a carrying case that contains all the materials needed to perform an analysis. It includes glassware, an electronic balance, reagents for 15 tests, video and written instructions, and all other components necessary for the 15 analyses. Eleven calibration photographs of more common substances (fuels, solvents, transformer oils, used motor oil, and others) are included in the kit. Additional calibration photographs can be obtained from the vendor.

Operating procedure:

1. Weigh 5 g of soil sample to be analysed;
2. Place sample into beaker;
3. Add solvent to sample in beaker;
4. Stir or mix sample and solvent to form an extract;
5. Pour extract into test tube;
6. Add catalyst to test tube;
7. Shake test tube for 2 min;
8. Compare test tube to colour ID card.

Dräger Detector Tubes

Device description: Detector tubes (Dräger) measure volatile gases and provide qualitative to semi-quantitative data for individual constituents or compound groups.

Operating procedure: Detector tubes) are glass tubes that change colour when exposed to specific gases. These consist of glass tubes are sealed and filled with a porous solid carrier material which is coated with colour reagents and changes colour when gas containing a specific analyte is drawn through the tube. The breakaway ends of the tube are snapped off and a known volume of air (usually 100 mL) is drawn through the tube at a fixed flow rate using a hand or electric pump. As air passes through the tube, a stain is produced by the reaction of target constituents with the reagents inside the tube. The length of the stain in the tube is proportional to the concentration of petroleum hydrocarbon in the gas sample (US EPA, 2016). Detector tubes provide readings in the parts per million (ppm) range. Tubes and performance are compound-specific, respectively.
The design of the short-term tube depends on the measurement task, particularly on the substance to be measured and the concentration range to be determined. There are several types of Dräger short-term tubes (Dräger, 2008) including:

- Tubes with a single indication layer,
- Tubes with one or more pre-layers plus an indication layer,
- Combination of two tubes,
    - tubes with connecting hoses,
    - tubes with a built-in reagent ampoule,
    - tubes for simultaneous measurement

A1.3.6. Field test kits based on Immunoassay

RaPID® BTEX/TPH Assay

Device description: RaPID® BTEX/TPH Assay is a tool originally developed by Strategic Diagnosis Incorporated (SDI) (Newark, DE), for measuring Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) and TPH in soil and water. The test complies with the EPA Method 4030 (EPA 1996) standards for the screening of soil samples for petroleum hydrocarbons. According to SDI and Modern Water, detection limits range between 0.9 to 30 ppm as the Total BTEX standard for soils. The test result is quantitative or qualitative and provides (1) rapid field-testing procedure for analysis of soil and water samples (2) quantitative data results with excellent analytical precision (3) results available in approximately 60 min (4) magnetic particle immunoassay (5) correlated to TPH methods (knowledge of fuel source required). Two kit sizes are available:30 Test Kit (tests up to 20+ samples) - 100 Test Kit (tests up to 80+ samples) (Modern Water 2013).

Operating procedure: Test kit components include: Antibody coated magnetic particles for analysis of 100 test tubes; Zero standard, wash, enzyme conjugate, colour development and stop reagents; Standards for 0.09, 0.35 and 3.0 ppm as total BTEX; Kit control as 2.1 ppm as total BTEX; Disposable test tubes.
Sample preparation: Soil samples require prior extraction using the sample extraction kit (sold separately). The sample extraction kit provides materials for 12 soil sample extractions with methanol.
Sampling time: Soil extraction time is typically two minutes per sample plus assay run time of approximately 60 minutes.

A1.3.7. Field test kits based on Turbidimetry

PetroFLAG® TPH test kit

Device description: The PetroFLAG® THP turbidimetric test kit is manufactured by Dexsil and follows US EPA documented protocol Method 9074 (US EPA, 2016; Quillen et al., 2010). The PetroFLAG® THP turbidimetric test kit quantifies both aliphatic and aromatic hydrocarbons in a range from C_8-C_{44}, and features a method detection limit range of 15 -2000 ppm (DEXSIL). The PetroFLAG® System extracts petroleum hydrocarbons in soil using an organic solvent mixture and the PetroFLAG® analyser emits light at a factory pre-set wavelength of 585 nm. The PetroFLAG® analyser is controlled by a low power consumption micro-computer with a preloaded operating program which is stored in EEPROM memory. The program cannot be lost regardless of battery condition. The PetroFLAG® analyser is powered by one 9 V alkaline battery (included). The battery should last for 18,000 readings. The meter stores two calibration curves in separate memory locations. These calibration curves can be independently updated, and the response factors can be changed without losing the calibrations. Response factors are indicated in the US EPA report (2001). The selected response factor is then used to calculate the correct concentration for the analyte of interest. Therefore, it is important to choose the response factor that is appropriate for the particular hydrocarbon or class of hydrocarbons present at the site (US EPA, 2001). The PetroFLAG® analyser comes with a reagents kit.

Operating procedure:

1) Extraction: A methanol-based (chloroflorocarbon-free) solvent is used to extract hydrocarbons from the soil sample. The sample is then agitated, and the soil is allowed to settle.
2) Filtration: The hydrocarbon extract is then separated from the soil and placed in solution (in a vial) until equilibration is reached.
3) Analysis: When the developing solution equilibrates, a reading is taken with the turbidity meter. The concentration of TPH in soil is directly proportional to the amount of petroleum hydrocarbons present in solution, and the value is drawn from the calibration curve. Ideally, group of 10 samples should be tested along with a blank and a calibration standard which is provided with the kit.

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