

An evaluation of field total petroleum hydrocarbon (TPH) systems

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Abstract

An evaluation of several field kits and petroleum hydrocarbon measuring systems was conducted. The field kits were the immunoassay based EnviroGard petroleum fuels in soil test kit (EnviroGard, Millipore Canada, Mississauga, Ont., Canada), the turbidimetric based PetroFlag hydrocarbon test kit for soil (Dexsil, Hamden, CT, USA), a DR/2000 field kit (Hach Company, Loveland CO, USA) employing colorimetric test procedures and a total organic carbon (TOC) analysis instrument (Dohrmann Division, Rosemount Analytical Inc., Santa Clara, CA, USA) using oxidation principles. These procedures were compared to the traditional technique of extraction of the petroleum hydrocarbons using trichlorotrifluoroethane (Freon 113) as the solvent and subsequent infrared (IR) analysis using a portable fixed wavelength analyzer (Buck Scientific, East Norwalk, CT, USA).

The EnviroGard kit was affected by the sample matrix. The soil type and the presence or lack thereof specific chemical components affected the capability to detect the petroleum hydrocarbon concentration. The PetroFlag soil test kit tended to generate results higher than the accepted concentration. The IR method was better capable of producing results similar to the expected concentration values of the prepared samples.

Results indicate that the total organic carbon analysis technique evaluated is best suited for samples containing dissolved hydrocarbons in water and is not a preferred procedure for water samples containing dispersed or floating oil. At low concentrations of 10 ppm and less, the TOC method and IR method have concentration values within a few parts-per-million (ppm) of each other, however, an examination of the trends in the results for all samples shows no similarity. This would indicate that the traditional extraction and infrared method and the total organic carbon method are not measuring the same parameter.

Finally, the colorimetric field kit was capable of quantifying the concentration of oil in water samples within limits. The results from the oil-in-water method built into the unit at the factory were not comparable with analysis carried out by the infrared technique. With specific methods for each oil incorporated into the spectrophotometer, the comparability of data increased significantly. Results generated by the kit are dependent upon the color and amount of the oil in the sample. The

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kit is best suited for dark colored oils and the water samples with concentrations in the range of 10 to 85 ppm by weight. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Emergencies Science Division has an on-going program to evaluate commercially available instruments, with the intent to review their applicability for on-site analysis of petroleum and chemicals in the environment.

The popularity of on-site analysis in general has continued to grow. This is due in part to the advantages of lower analysis costs and the reduced turn around time required to obtain results. Spills of petroleum and petroleum products have traditionally been the most commonly reported type of spill incidents. As such, field analysis procedures for petroleum hydrocarbons have existed for some time. Most of these use instruments that measure volatile organic hydrocarbons [1,2] or adaptations of the procedure from standard oil and grease and petroleum hydrocarbons [3]. The Montreal Protocol, calling for the reduction in the use of ozone depleting substances such as trichlorotrifluoroethane (Freon 113), has resulted in the decrease in popularity of the aforementioned method due to environmental concerns, its lack of availability and a substantial escalation in the cost of the reagent. To meet environmental regulatory requirements, the need for field results comparable to laboratory data has increased. This in turn has produced improvements in existing field methodologies and promoted the development of alternatives to the use of Freon 113 solvent.

Petroleum hydrocarbon analysis in the laboratory and field is an evolving process. No specific definition exists of what constitutes total petroleum hydrocarbon. Instead, as technology changes so does the ability to detect, isolate, identify and quantify very specific chemical compounds in petroleum products [4]. With this, the understanding of the complexity of petroleum products and fuels improves, but the meaning of the term “total petroleum hydrocarbon” becomes ambiguous. As a result many different technologies have been employed to detect and quantify the amount of petroleum hydrocarbons present in samples. Listed in Table 1 are some general examples of commercially available portable equipment for measuring petroleum hydrocarbon content. The table includes the product and manufacturer name, its detection technique, information on the methods compliance with ozone depleting substances guidelines, the sample media and the TPH fraction, the method actually detects.

2. Objectives

The objectives of this project are to provide a review of commercial methodologies and instruments for measuring petroleum hydrocarbons in the environment, assess their adaptability for use in the field, and to compare the results of those methods to results obtained by traditional methods of analysis.

Table 1
A summary of commercial portable petroleum measuring equipment

Instrument (manufacturer)	Detection technique	ODS compliant ^a	Media	TPH fraction
PetroFlag (Dexsil)	Colorimetric	Yes	Soil	Fuel, oil, grease
DR/3000, DR/2000, DR/700 (Hach)	Colorimetric	No	Water	Trichloroethane extractable
Field Test (H.E.L.P)	Colorimetric	Yes	Soil/water	Aromatics
Petosense PHA-100 (FCI)	Fiber-optic probe	Yes	Water	Aromatics and water soluble
Field Fluoro-Tec (St. John)	Fluorometry	Yes	Water	Aromatics
10-AU (Turner)	Fluorometry	Yes	Water	Aromatics
Diagnostix	Immunoassay	Yes	Soil/water	BTEX
Dtech (EM Science)	Immunoassay	Yes	Soil/water	BTEX
EnSys	Immunoassay	Yes	Soil/water	BTEX
ViScreen (Hach)	Immunoassay	Yes	Soil/water	BTEX
EnviroGard (Millipore)	Immunoassay	Yes	Soil/water	BTEX
Portable Workstation (Quantix)	Immunoassay	Yes	Soil/water	BTEX
Disposable IR Cards (3M)	Infrared	Yes	Water	Hexane extractable
Film Plate Cell (Buck)	Infrared	Yes	Water	Hexane extractable
TPH Analyzer (GAC)	Infrared	Optional	Soil/water	Freon 113 or hexane extractable
Minicon-THC (Grabner)	Infrared	Optional	Water	Freon 113 or hexane extractable
Oil Content Analyzer (Horiba)	Infrared	No	Water	Freon 113 extractable
Oil-in-water Analyzer (Infracal)	Infrared	Yes	Water	Hexane extractable
Total Hydrocarbon Analyzer (Buck)	Infrared	No	Soil/water	Freon 113 extractable
Oil and Grease SPE Disks (CPI)	Solid phase extraction	Yes	Water	Hexane extractable
Empore Disks (Baker/3M)	Solid phase extraction	Yes	Water	Hexane extractable
Speeddisk (Baker)	Solid phase extraction	Yes	Water	Hexane extractable
EnvirElut (Varian)	Solid phase extraction	Yes	Water	Hexane extractable
TOC Analyzer (Sievers)	Photocatalytic oxidation	Yes	Water	All organics
Anotoc (SGE)	Photocatalytic oxidation	Yes	Water	All organics

^a Compliant with federal “ozone depleting substances (ODS)” guidelines.

3. Procedures

The following paragraphs describe the steps taken to prepare the samples and the methods used to determine the petroleum hydrocarbon content. The evaluation program was carried out at different times over an extended time period. The equipment was tested using either a soil or water sample matrix, as intended by the manufacturer.

Both the EnviroGard and PetroFlag kits are designed for soil samples. Two types of soil samples were used. These included actual environmental samples from a historic spill site and prepared samples of diesel fuel mixed with sand. The diesel fuel-in-sand samples were prepared using 8 wt.%, artificially weathered diesel fuel. The source of the diesel fuel is described in Fingas et al. [5] and Walton et al. [6]. The weathered sample was generated by rotary evaporation of the original fuel using an established method [7]. The washed, all-purpose sand is a commercially available product sold under the name Sakret (King Paving and Materials Ltd., Paris, Ont., Canada). Samples were prepared by adding a known volume of fuel to a weighed amount of sand. The density of the oil was used to convert the volume to weight. Five samples were prepared over the concentration range of 0–836 mg/g.

The EnviroGard kit was used in accordance with the manufacturer's instructions. The measurement range of the kit is 5–1250 ppm. Determination of TPH, with the PetroFlag kit, was also done using the manufacturer's instructions. The measurement range of the kit is 10–2000 ppm. These were compared against a modified version of the ASTM method D 3921-85 (reapproved 1990), standard test method for oil and grease and petroleum hydrocarbons in water [3], commonly known as an IR method. Readings were taken, following the manufacturer's instructions, using a fixed wavelength model 404 IR analyzer (Buck Scientific, East Norwalk, CT, USA). The measurement range of the IR is 2–20 000 ppm.

The TOC and Hach kit were examined using water samples. Like the soil test kits, the overall capabilities of both approaches as suitable field techniques for the determination of oil-in-water concentration are compared to those of the traditional solvent extraction and infrared analysis method.

Total organic carbon analysis was performed using a commercially available instrument, the Dohrmann DC-80 (Rosemount Analytical Inc., Santa Clara, CA, USA). The evaluation procedure involved determining the amount of oil in the water samples generated in a test vessel. Analytical procedures were based on the manufacturer's instructions and the ASTM method D 4839-94 standard test method for total carbon and organic carbon in water by ultraviolet, or persulfate oxidation, or both, and infrared detection [8]. In summary, testing was carried out using a laboratory bench-top instrument having an operating range of 0–4000 ppm. There are three separate settings over the 0–4000 ppm span of which it is necessary to select the optimal range for the samples requiring analysis. Each setting is individually calibrated using a prepared standard consisting of the certified primary standard potassium hydrogen phthalate (Fisher Scientific, Nepean, Ont., Canada) dissolved in water.

For sample analysis, a prescribed volume of the water sample is directly injected into the reaction module of the instrument. The specific sample volume required depends upon the range employed. For analysis over the 100–4000 ppm span, a volume of 40 μ l is used, while the 10–800 and 0.1–160 ppm span, a 200 and 1000 μ l volumes are used, respectively. Once in the reaction module, the presence of ultraviolet light, a potassium persulfate solution and

oxygen gas oxidize the carbon in the sample to form carbon dioxide gas. The oxygen carrier gas transfers the carbon dioxide to an infrared detector where the sample's concentration is determined by comparing its response to that of the calibration standard. Results are printed in units of parts-per-million by weight.

Solvent extraction and infrared analysis was carried out using Freon 113, or more appropriately trichlorotrifluoroethane (Fisher Scientific, Nepean, Ont., Canada), and the Buck model 404 fixed wavelength infrared analyzer. The procedure itself is based on the manufacturers instructions and the ASTM method D 3921-85 (reapproved 1990), standard test method for oil and grease and petroleum hydrocarbons in water [3]. Calibration curves are prepared by measuring the absorbance of a series of oil-in-solvent standards accurately prepared by dissolving known amounts of an oil into Freon 113. These standards covered the range of 0–1000 ppm. For the standards, a medium to light crude oil, Alberta Sweet Mixed Blend (ASMB) was selected. It is commonly used by the Emergencies Science Division as a reference oil. In addition several standard solutions of diesel fuel and hydraulic oil (Esso XD3-10) in trichlorotrifluoroethane were prepared to examine the capability of the infrared analyzer. For this test series the standards were prepared to known concentrations by weight in micrograms (μg) per gram (g) of solvent or parts-per-million (ppm) by weight. To measure oil concentration, the water sample was extracted with a known amount of solvent and the absorbance of the solvent measured on the analyzer. The absorbance of the sample extract was compared to those of the standards to calculate the concentration of the extract then the weight of the water sample was used to determine the oil-in-water content.

Labware and reagents used in the experiments were obtained separately. The reagents were of high quality and the labware was suitably cleaned and prepared.

Experimental oil-in-water samples were generated as follows. Three carboy apparatus were setup and run concurrently. The test program was performed using three oils, Alberta Sweet Mixed Blend, diesel fuel and hydraulic oil (Esso XD3-10). The properties of these oils can be found in Jokuty et al. [9]. The entire apparatus has been setup for several years, thus the water has had a prolonged exposure to the oil. A 20 l, oil resistant, plastic carboy was filled with deionized water and placed on a mechanical stirring unit with a 5 cm stirring bar. A spigot was located on the carby at approximately one-third of the distance up from its base. When the apparatus was set-up, a weight of 20 g of oil was placed onto the surface of the water and then the vessel was capped and the contents of the vessels were vigorously stirred for days to allow dissolution of the oil into the water column. For this experiment, prior to applying any mixing energy, a 100 g sample of the water was withdrawn for analysis. An additional 20 g of oil was added and the mixing energy was then applied for a 24 h period. Water samples were collected at noted times during and following the mixing period. The 100 g samples were collected from the carboys in wide mouth glass bottles. The contents of the sample bottles were allowed to settle permitting any mechanically dispersed oil to rise to the surface of the water. For the total organic carbon analysis, the water sample was analyzed without any type of sample preparation. An appropriately sized syringe fitted with a large gauge #23G1 needle (Becton Dickinson and Company, Rutherford, NJ, USA) was inserted into the water sample such that an aliquot was obtained from 2 cm below the surface. In order to obtain consistent results and stay within the limitations of the instrument itself every effort was made to avoid oil floating on the surface from coming into contact with the outside of the syringe. For the infrared analysis, the remainder of the contents

of the sample bottle, including the floating oil, was transferred to a separatory funnel and extracted with a known amount of solvent. The absorbance of the oil-in-solvent was then measured on the analyzer and used to calculate the oil-in-water concentration.

The Hach DR/2000 portable kit (Hach Company, Loveland, CO, USA) is a commercial product designed to quantify various contaminants in aqueous samples. The kit contains a manual, labware and a small UV–VIS spectrophotometer and has more than 120 preprogrammed factory calibration curves. By following the test procedures outlined in the manual and using the spectrophotometer, the concentration of the chemical can be determined. The detection principle is based on colorimetric techniques. One such Hach method is #8041, oil-in-water. The method calls for a 350 ml volume of a water sample to be extracted with 35 ml of 1,1,1-trichloroethane. The color of the extract is compared to the factory installed calibration curve after the instrument has been blanked with fresh 1,1,1-trichloroethane. A few seconds after the sample extract has been placed in the unit, the concentration of the original water sample is displayed on the unit. This value was calculated by the instruments software assuming the procedure was followed exactly. The factory calibration curve was prepared using a California crude oil. New calibration curves can be input into the memory of the unit to expand its capabilities or the instrument can be used as an colorimetric absorbance meter providing only an extract's absorbance value.

The evaluation of the kit included a review of the factory oil-in-water procedure as well as the capability of the kit as a whole. A series of oil-in-solvent standards over the concentration range of 0–1000 ppm, by weight, were prepared using ASMB, diesel fuel and hydraulic oil in 1,1,2-trichloro-1,2,2-trifluoroethane as described earlier. The factory method was evaluated using the prepared standards and then the standards were used to develop new calibration curves for each oil type. The extracts from the experimental water samples described in the previous section were measured using the appropriate calibration curve based on oil type. The concentration of the water samples was determined using the concentration values displayed on the DR/2000 and back calculating to account for solvent and water dilution weights. These concentration values were compared to those obtained from the IR and TOC analysis.

4. Results

Results are listed in Table 2, TPH Results for soil samples, for the concentration values obtained for the prepared diesel fuel-in-sand samples and the environmental samples using the three methods of analysis, IR, PetroFlag and EnviroGard. When warranted, repeat analysis was carried out and included in the table.

Table 3 lists the concentrations of the prepared oil-in-solvent standards and their corresponding absorbance values as measured using the Hach DR/2000 colorimetric spectrophotometer and the Buck model 404 infrared analyzer. The DR/2000 colorimetric absorbance measurements were made at 450 nm wavelength and the unit displays absorbance values to three decimal places, e.g. 0.001. The Buck 404 infrared analyzer is fixed at a wavelength of 2924 cm^{-1} (3420 nm) and displays absorbance values to three decimal places.

The absorbance of select diesel fuel-in-solvent and hydraulic oil-in-solvent standards was measured on the infrared analyzer. These were the 600 and 1000 ppm standard for

Table 2
IR, PetroFlag and EnviroGard TPH results for soil samples

Sample	Solvent extraction and IR quantification ($\mu\text{g/g}$)	Dexsil PetroFlag color analyzer kit (mg/g)	Millipore EnviroGard immunoassay kit ($\mu\text{g/g}$)
Diesel-in-sand, 0 $\mu\text{g/g}$	16	0	0
	11 ^a		0
Diesel-in-sand, 8 $\mu\text{g/g}$	18	0	0
	17 ^a		0
Diesel-in-sand, 83 $\mu\text{g/g}$	68	91	0
	17 ^a		0
Diesel-in-sand 419 $\mu\text{g/g}$	342	542	0
	46 ^a		50 < x < 250
Diesel-in-sand 836 $\mu\text{g/g}$	692	1327	0
	131 ^a		50 < x < 250
S623-1125	3545	>20000	0
	533 ^a		0
S623-1150	656	3810	0
	310 ^a		0
S623-1235	3781	11450	0
	2146 ^a		0
S623-1300	>20000	>20000	0
	>20000 ^a		0
S623-1645	2205	8370	0
	652 ^a		0
S623-1655	200	3270	0
	123 ^a		0
S623-1845	12	1227	0
	11 ^a		0

^a Solvent extract was filtered through silica gel.

each oil type. The absorbance values of the diesel fuel-in-solvent standards were 1.404 and >2 for the 600 and 1000 ppm standards, respectively while the absorbance values of the hydraulic oil standards were 1.437 (600 ppm) and >2 (1000 ppm), respectively. Using the absorbance versus concentration calibration curve of the ASMB-in-solvent standards, the 600 ppm diesel fuel-in-solvent standard was determined to be 633 and the 600 ppm hydraulic oil-in-solvent standard was 648 ppm. The relative errors of these concentration values are 6 and 8% for the diesel and hydraulic standards, respectively. An absorbance of >2 indicates a reading in excess of the upper limit of the instrument. The values were included for information purposes but were not used to calculate the correlation coefficient.

Table 4 lists the concentrations of the prepared oil-in-solvent standards and their corresponding concentrations as displayed by the Hach DR/2000 colorimetric spectrophotometer. The results for the factory method are from the ASMB-in-solvent standards. The results reported are average values of two measurements of the same extract. The relative spread of the results was less than 10% with the exception of ASMB-in-solvent standards with concentrations less than 10 ppm. There is no data available for the diesel and hydraulic standards at that concentration and the ASMB had relative errors in excess of 100%.

Methods were developed in input into the spectrophotometer for each oil type. The absorbance of select diesel fuel-in-solvent and hydraulic oil-in-solvent standards was

Table 3
Absorbance readings of oil-in-solvent standards^a

Concentration (ppm)	Colorimetric absorbance of ASMB-in-solvent standard	Colorimetric absorbance of hydraulic oil-in-solvent standard	Colorimetric absorbance of diesel fuel-in-solvent standard	Infrared absorbance of ASMB-in-solvent standards
0	0	0	0	0
0.1	−0.013	Not measured	Not measured	0.001
1.0	−0.013	Not measured	Not measured	0.005
10.0	−0.008	0	0	0.026
40.0	0.008	0.001	−0.001	0.094
200.0	0.141	0.005	0	0.458
600.0	0.516	0.015	0.002	1.326
1000.0	0.986	0.024	0.004	>2
Correlation coefficient	0.9973	0.9996	0.9673	0.9999

^a Solvent is 1,1,2-trichloro-1,2,2-trifluoroethane.

Table 4
Concentration readings of oil-in-solvent standards

Concentration (ppm)	Colorimetric concentration using ASMB-in-solvent method (ppm by weight)	Colorimetric concentration using hydraulic oil-in-solvent method (ppm by weight)	Colorimetric concentration using diesel fuel-in-solvent method (ppm by weight)	Colorimetric concentration using factory method (ppm by weight)
0	0	0	0	0
0.1	10	<IDL ^a	<IDL ^a	0
1.0	6	<IDL ^a	<IDL ^a	0
10.0	20	25	727	0
40.0	51	56	759	10
200.0	209	234	832	80
600.0	582	621	1000	300
1000.0	1000	1000	1000	560

^a <IDL: less than instrument detection limit = 0 ppm.

Table 5
A summary of the experimental water sample concentration results

Sample no.	Oil type	Sample description	Infrared oil-in-water concentration (ppm by weight)	Colorimetric oil-in-water concentration (ppm by weight)	Total organic carbon oil-in-water concentration (ppm by weight)
1	Water	DI water	0	–	7.5
2	Diesel	No mix time	1	139	1.8 ± 26%
3	Hydraulic	No mix time	1	313	3.4
4	ASMB	No mix time	1	0	3.6
5	Diesel	5 min mix time	11	306	1.8
6	Hydraulic	5 min mix time	966	453	20.4 ± 46%
7	ASMB	5 min mix time	146	200	4.9 ± 26%
8	Diesel	5 min settle time	3	406	3.6
9	Hydraulic	5 min settle time	377	438	6.1 ± 13%
10	ASMB	5 min settle time	2	1	9.8
11	Diesel	0.5 h settle time	0	320	2.7
12	Hydraulic	0.5 h settle time	2	70	5.3
13	ASMB	0.5 h settle time	2	1	9.1
14	Diesel	1 h settle time	0	318	2.3
15	Hydraulic	1 h settle time	28	106	5.5 ± 18%
16	ASMB	1 h settle time	1	1	9.3
17	Diesel	2.5 h settle time	2	307	2.2
18	Hydraulic	2.5 h settle time	6	67	5.1
19	ASMB	2.5 h settle time	2	2	9.1
20	Diesel	4.5 h settle time	0	284	2.4
21	Hydraulic	4.5 h settle time	4	108	4.8
22	ASMB	4.5 h settle time	0	2	9.5
23	Diesel	6.5 h settle time	1	312	2.4
24	Hydraulic	6.5 h settle time	2	237	5.0
25	ASMB	6.5 h settle time	0	0	9.8
26	Diesel	24 h settle time	0	390	3.1
27	Hydraulic	24 h settle time	3	41	5.6
28	ASMB	24 h settle time	1	0	9.6

measured on the various other colorimetric methods input into the unit. For example, the 600 and 1000 ppm hydraulic oil-in-solvent standards were measured using the factory method and ASMB method while the 600 and 1000 ppm diesel fuel-in-solvent standards were measured on the factory oil-in-water method. The concentration displayed on the unit for the diesel fuel and hydraulic standards, as determined by the factory method, were 0 and 10 ppm for the 600 and 1000 ppm standards, respectively regardless of oil type. The ASMB method gave concentration values of 750 and 1000 ppm for the hydraulic oil standards of 600 and 1000 ppm.

Table 5 lists the oil-in-water concentration values of the experimental water samples using the infrared, colorimetric and total organic carbon methods. The TOC values are averages of three measurements. With the exception of those S.D. included in the table, the S.D. of the TOC results was <10%. The infrared and colorimetric results were consistent and influenced only by the reading error (± 0.002) of the absorbance. The infrared and colorimetric concentration values of the water samples are calculated from comparison to the absorbance and concentration of the oil-in-solvent standards. These values are then adjusted to account for the amount of solvent used to extract the oil and the initial weight of the water sample. The final oil-in-water concentration data is presented in units of ppm by weight. The TOC method provided a result in ppm by weight. To equate the organic carbon concentration to an oil-in-water concentration the TOC value was adjusted using a typical factor of 85%. That is to say, a typical oil contains 85% carbon [10].

5. Discussion

Both the EnviroGard and PetroFlag kits examined in this study claim to be able to quantify the amount of petroleum hydrocarbons in soil. Testing was carried out using the manufacturers' instructions, thus the sample preparation and detection principle differs for each method. A list allowing the comparison of the TPH results is presented in Table 2. The results make it possible to compare the responses of different technologies evaluated under the same conditions. Two separate types of samples were examined. The first samples were a series of five prepared diesel fuel-in-sand samples with known concentrations while the second set of seven samples were samples collected from a contaminated site. The purpose of the prepared samples was to determine the capability of the various procedures to accurately quantify the amount of petroleum hydrocarbons in a soil sample. Prewashed sand was used as the soil matrix and should represent an optimal situation, as sand usually is the easiest matrix to remove contaminants from. A weathered diesel fuel was used as the contaminant to simulate conditions commonly found in the field.

The samples from the contaminated site provide information on the capability of the field kits when dealing with difficult samples, where the fuel has had an opportunity to weather and adsorb into the sample matrix. The soil itself is a mixture of sand, gravel and organic material which lends to the difficulty of analysis. None of the samples used in this portion of the experiment were analyzed by standard laboratory methods. However, several other samples, collected in the same area, did undergo laboratory analysis. Their results are included here for information purposes only. Laboratory analysis on the sample from the same area as the environmental samples S623-1125–S623-1300 found a petroleum

hydrocarbon concentration of 227 $\mu\text{g/g}$. No purgeable hydrocarbons were detected. Samples S623-1645 and S623-1655 were collected in an area where laboratory analysis of other samples showed petroleum hydrocarbon concentration of between 1710 and 4830 $\mu\text{g/g}$. Again, no purgeable hydrocarbons were detected in the samples.

The results from the EnviroGard immunoassay kits showed that with the exception of the two prepared diesel fuel-in-sand samples having the highest concentration, the immunoassay kits could not detect the presence of the petroleum hydrocarbons. Testing was repeated to confirm results, with both sets of analysis producing similar responses. The weathered diesel used in the prepared samples and the natural weathering of the fuel in the environmental samples has resulted in the inability of these kits to extract sufficient material to produce accurate responses. As described earlier, the low level of lighter components in the fuel and the soil matrix affected the capabilities of EnviroGard kits. The kits are marketed as a semi-quantitative tool. The advantages of these kits are that they can significantly reduce the time and cost of analysis and this technology is an all-inclusive kit. A kit can analyze a maximum of 17 samples. Estimated cost of a complete kit, the sample preparation labware and solvent is US\$ 450. A one-time purchase of reusable pipettes would be an additional US\$ 350.

The PetroFlag kit appears to have the capability to deal with weathered fuels. From the results of the prepared samples, it can be seen that the PetroFlag methodology can differentiate between different levels of contamination. Results from the field kit are higher than the accepted concentration of prepared samples. The soil composition and matrix of the environmental samples had little effect on the capability of the kit to obtain reasonable data. Like the prepared samples, the results are higher than those from the other test procedures. Sample S623-1846 is a background sample with low petroleum hydrocarbon content. The result for that sample is a false positive. It is not uncommon for field kits to generate high results as they are sometimes designed to err on the side of caution. The reaction in the test vessel produces turbidity in proportion to the amount of hydrocarbons. Interferences such as suspended particulate can affect results. In general the kit was capable of detecting and approximating the concentration of petroleum hydrocarbons in soil. The PetroFlag test kit is entirely self contained, easy to use, has a purchase price of US\$ 700, and can analyze ten samples before requiring additional stock. Replacement reagent packages for ten samples are \sim US\$ 100.

The infrared test procedure is not a commercially available field kit. In fact, it was only with the development of portable IR spectrometers, that this laboratory procedure has been made field portable. Necessary equipment and reagents, in addition to the IR, must be purchased separately. Costs for these can be as high as US\$ 1000. The solvent employed in the procedure, trichlorotrifluoroethane, is an ozone depleting substance and regulated under the Montreal Protocol. This has caused a drastic increase in the solvent price (US\$ 500 per 41 bottle), if it is available at all. The cost of the spectrometer is US\$ 8000, however the prices have begun to slowly decrease with increased market competition.

A review of the results shows that the procedure can satisfactorily detect petroleum hydrocarbons in soil and appears to have the lowest detection limits of the three methods evaluated. Two separate runs were performed. In the first set (results are indicated by an asterisk (*)) the extracts were filtered through silica gel, as described in the procedure. The purpose of the silica gel is to remove the polar compounds, thought to be non-petroleum hydrocarbons, from the extract so that the final results reflect a true petroleum hydrocarbon

value. As filtration through the silica had the effect of inconsistently reducing the results by up to 75%, the second set of extracts were not filtered. Measured petroleum hydrocarbon concentrations were generally about 80% of the expected value for the prepared samples. Results from the environmental samples showed similar trends between the IR method and the PetroFlag kit, however the IR procedure generated numerically lower values. Results from the IR procedure were closer to the expected hydrocarbon concentrations based on the laboratory results of other samples collected in the area. This is not unexpected, as experience has shown the solvent employed possesses above average extraction capability in comparison to the solvents from the other kits. Unlike the other kits, which have a subsequent reaction in the detector portion of the procedure, the accuracy of the IR test is primarily dependent on the extraction efficiency of the solvent.

The traditional solvent extraction and infrared method used in these experiments is a mainstay for both the laboratory and field analysis of environmental samples containing petroleum hydrocarbons. The procedure calls for the use of Freon 113 to extract the oil from the sample matrix. The results from previous work [11] showed that the Freon 113 extraction and infrared detection method generated results similar to that of laboratory gas chromatograph analysis for water samples. The reasons for the historical popularity of Freon 113 were its high capability to extract oil from the sample matrix and its “invisibility” in the region of the infrared spectrum used to detect and quantify petroleum. With the introduction of regulations controlling ozone depleting substances, use of Freon 113, an ozone depleting substance, is being phased out towards its eventual elimination from use. This has caused a drastic increase in the solvent price over the past few years from US\$ 25–500 per 4 l bottle. In time it may not be available at all. As a result, alternative methods and modifications to existing methods have been proposed for the analysis of oil in samples. However, there is a reluctance on the part of the scientific community in making a decision to alter detection methods. This is due in part to the variations in the results generated using different techniques and the variation in the performance and reliability of alternative procedures.

There are other operational limitations to the infrared method in addition to the solvent issue. The analyzer is not part of a commercially available portable field kit and supporting labware must be supplied. The upper detection limit is 900 ppm of oil-in-solvent while the lower detection limit is 0.5 ppm oil-in-solvent. A review of the concentration data from the infrared analysis of the oil-in-solvent standards shows that a single oil may not be suitable as a universal calibration standard. The concentration of the 600 ppm hydraulic and diesel fuel standards, as determined using the ASMB calibration curve, were 648 ppm (8% relative error) and 633 ppm (6% relative error), respectively. This is normally well within the bounds of acceptable error for a field screening test, however, it may become important if the field analysis was being employed to obtain data to ensure regulatory compliance. The reason for the differences in the absorbance of the oils can be explained. Infrared spectrometers detect the energy of the carbon to hydrogen (C–H) bonds at a wavelength of $\sim 2940\text{ cm}^{-1}$ and use this to quantify the amount of oil in a sample. Oils are made up of predominantly carbon and hydrogen. Oils contain many chemical compounds and the different compounds are often categorized into hydrocarbon groups based on chemical structure [12]. The hydrocarbon groups are saturates, aromatics, asphaltenes and resins. The proportion of each hydrocarbon group varies with each oil. A decrease in the relative amount of one fraction implies a corresponding increase in another fraction. It is the saturate

fraction of oils which is identified as containing most of the carbon to hydrogen bonds. As the saturate fraction decreases the amount of carbon and hydrogen bonds in the oil generally decreases because the other fractions contain more carbon-to-carbon bonds. This theory is supported by data from Jokuty et al. [9]. The weight percent saturate fraction of the ASMB (65%), diesel fuel (78%) and an automotive lubricating oil (77%) correspond with the trend in absorbance values for the respective oil-in-solvent standards. That is, the ASMB has the lowest saturate fraction and absorbance value.

From the results for the correlation coefficients shown in Table 3, it appears that the new, oil specific, Hach DR/2000 colorimetric methods have a linear response over the 0–1000 ppm concentration ranges. However, this is somewhat misleading. Many of the absorbance values were close to zero and could not be distinguished from background. The negative values for the ASMB-in-solvent standards between 0.1 and 10 ppm is the reason, the hydraulic and diesel fuel standards at that concentration range were excluded and show that this colorimetric technique is not suitable for low concentrations. The entire range of absorbance values for the diesel fuel standards is very small and not significantly different from the background zero value. As such, the diesel method cannot be supported based on the “best practices” of analytical chemistry. Although, the ranges of the absorbance values for the hydraulic oil and ASMB standards are better than those of diesel fuel standards, the previous statements made about the diesel method holds true for the hydraulic standards with concentration <200 ppm and ASMB standards <40 ppm. The performance of the Hach kit is highly dependent on the color of the extract. Absorbance ranges from 0–2 with this spectrophotometer. High concentration or dark extracts with absorbance values greater than two can be diluted until within the working range. At low concentrations, the absence of color in the extract limits, the ability of the spectrophotometer to differentiate between the sample and background absorbance.

In Table 4 the concentration results of the oil-in-solvent standards support the points of the previous paragraph. In addition, the results in the table and the data from the work where an oil-in-solvent concentration was measured using another oil-in-solvent calibration curve shows the low versatility of each method. The Freon 113 solvent used to prepare all of the oil-in-solvent standards differs from the solvent stipulated in the factory procedure. This would have some impact on the factory method results. The differences in the color of the California crude oil used to calibrate the spectrophotometer and ASMB would account for the mediocre concentration results for the ASMB standards using the factory method. The results of the hydraulic and diesel fuel standards using the factory method and those of the hydraulic oil using the ASMB method show the same poor comparison as that of the results of ASMB standards with the factory method. It should be pointed out that the instruction manual for the Hach DR/2000 clearly indicates the limits of the factory method. To ensure some level of accuracy, a separate calibration curve would have to be prepared for each oil type.

Several aspects are highlighted in the water sample results shown in Table 5. Note that the colorimetric calibration curves just discussed were used to calculate the colorimetric concentration values listed. The relationship of the colorimetric data to the infrared data reinforce the limitations of the Hach field kit to quantify oil-in-water concentrations. The concentration values for the diesel samples were consistently much higher than those from IR analysis. As well, they do not show similar trends in terms of their relative relationship to each other over the sampling period. Extract from water samples often does possess some

amount of turbidity unlike oil-in-solvent standards prepared by serial dilution. Because of the narrow range of absorbance for the nearly colorless diesel-in-solvent calibration standards, the turbidity interfered with the samples absorbance and inflated the concentration results. The bolder color in the hydraulic oil was responsible for the slight improvement in correlation with IR data in comparison to the diesel samples. Of interest is the hydraulic oil samples # 6 and # 9. These water samples had high oil concentration as determined by IR methods yet the colorimetric techniques did not show the same responsiveness to differences in concentration. There was good correlation between the results for colorimetric and IR method for the water samples containing ASMB however, at the higher concentrations, the correlation is less. The resolution of the colorimetric method, which allows it to differentiate between solutions with similar concentration, is less than that of the IR method.

The results of the water samples analyzed by the total organic carbon method are more challenging compared to the IR method. Certainly, at low concentrations of <10 ppm oil-in-water, the two methods appear to correlate well. The operational requirement of having to inject a maximum of 1 ml of sample into the instrument was a significant limitation. The syringe and needle fitting make sampling mechanically dispersed or floating oil difficult and there is a tendency to be selective as to where the aliquot is collected which may in turn result in a sampling bias.

During analysis of the samples it was observed that the instrument was very prone to errors when samples containing oil droplets or bulk oil were injected. This is evidenced by the sample concentration results in Table 5 with high standard deviation. Often, runs in which bulk oil was injected, failed due to long run time errors. Effort was made to collect an aliquot from a location with no oil droplets and/or floating oil. There is some doubt if the oxidation process in the TOC instrument possess, the ability to convert the carbon in the oil to carbon dioxide. Each oil type showed consistent TOC results for all samples collected after the mixing energy was stopped. Diesel-in-water samples measured 2.6 ± 0.5 ppm, hydraulic oil-in-water sample results were 5.3 ± 0.4 ppm and ASMB-in-water results were 9.5 ± 0.3 ppm for all samples over the 24 h settling period. One would expect a slow decrease in the oil concentration with time as more oil returned to the surface of the water. Total organic carbon analysis has a long history and was developed to monitor the quality of water and waste-water. It is used in conjunction with biological oxygen demand and chemical oxygen demand data to obtain a complete picture of the oxidation state of the organic carbon in water [13]. The organic carbon in water takes many forms. These include natural organic compounds such as proteins (40–60%), carbohydrates (25–50%) and lipids (10%) as well as synthetic organic compounds such as surfactants (including hydrocarbon oils), pesticides, cleaning solvents and trihalomethanes all in low concentrations [14]. This information would lead to the conclusion that the TOC method and IR method are measuring related but not the exact same parameter. Total organic carbon analysis is quantifying the oil components soluble in the water column and is not well suited for oil detection.

6. Conclusion

Results from the EnviroGard petroleum fuels in soil test kit showed it to be the least responsive and appeared to be significantly effected by the sample matrix. The PetroFlag

hydrocarbon test kit for soil was less affected by the sample matrix but generated high results. Both of these commercially available test kits are relatively user friendly. The modified solvent extraction and IR method appears to be the most sensitive method. Results are more likely to represent the real hydrocarbon content of a sample, however the procedure requires expensive reagents and instruments, and some training.

Instructions provided by the manufacturer for each of the procedures were found to lack sufficient measures to ensure adequate quality control over results. Additional steps should be taken by the analyst such as the inclusion of soil blanks.

Preliminary screening tests were carried out to assess the suitability of two commercially available instruments as analytical tools for measuring petroleum contamination. Although limitations exist, results show that the Hach DR/2000 field kit employing a solvent extraction procedure and colorimetric detector could produce results comparable to the traditional method of Freon 113 solvent extraction procedure with an infrared detector during field applications at oil spills. The method provided by the factory was not adequate, however, the instrument can be easily adapted to include methods for each specific oil type. The field kit is best suited for water samples containing dark colored oil in concentrations of generally 10–85 ppm.

Results from the evaluation of total organic carbon analysis procedures showed this technique was not an optimal method for measuring oil-in-water concentrations at oil spills. Operational considerations such sample size have to be overcome in order to modify this laboratory procedure to a field method. Oil droplets and/or bulk oil interfered with analysis resulting in errors. This technique is best suited for water samples without dispersed or floating oil and may be applied to monitor low petroleum concentrations.

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