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SOLVENT-FREE DETERMINATION OF TPH IN SOIL BY NEAR-INFRARED REFLECTANCE SPECTROSCOPY

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ABSTRACT

Public awareness of environmental concerns are on the increase, and thus, safety standards have become more stringent, and far more analyses are required. Due to extensive oil exploitation, refining and transportation, oil pollution has become a major source of water and soil contamination. Although a number of standard procedures exist to quantify total petroleum hydrocarbons (TPHs) in soil, they all require time- and labor-intensive sample preparation, and most use per-halogenated solvents. Therefore, a feasibility study was undertaken to test the possibility of using near-infrared reflectance spectroscopy (NIRS) for direct determination of oil contamination in soil. Based on a set of no. 43 samples spiked with known and independently confirmed TPH contamination of 0.05 to 2.19 wt% (using liquid-solid extraction and US-EPA method 418.1) a chemometric model was developed. The regression model fulfilled the following criteria for the reference data: validation coefficient $r^2 \geq 0.929$ and root-mean-square error of validation ≤0.177. A set of no. 26 field samples contaminated with weathered crude oil (≈0.1-5%) were analyzed by NIRS and conventional methods (i.e., extraction and US-EPA method 418.1). A correlation factor of $r^2 \geq 0.928$ with a standard deviation of the absolute differences between true and predicted values of ≤0.251 was obtained.

Keywords: NIRS, quantification, soil, TPH.

1 INTRODUCTION

In a growing, industrialized world, accidental and/or industry-related contamination of vast areas threatens the environment as well as humans and wildlife daily. Today, as a result of oil exploration, production, refining and transportation, petroleum hydrocarbons have become one of the most frequent sources of pollution in the environment. In particular, in an oil-producing country like Kuwait, oil pollution is the order of the day. According to the guidelines for drinking-water quality of the World Health Organization [1], petroleum hydrocarbons contain numerous toxic substances, and long-term exposure, especially to the polyaromatic hydrocarbon fraction, creates a high risk for cancer. Therefore, ascertaining which areas are polluted with oil and estimating the extent of the contamination is of great public concern. For instance, to prevent leaching of toxic hydrocarbons originated from oil contaminated soil into the ground water Wyoming Department of Environmental Quality recommends a clean-up level of ≤0.23wt% for diesel or crude oil contaminated soil [2].

A number of standard procedures, such as those of the United States Environmental Protection Agency (US-EPA) and American Society for Testing and Materials (ASTM), regulate the quantification of total petroleum hydrocarbons (TPHs) in soil and water [3–6], in order to ensure reproducibility and reliability. Usually, TPH analysis in soil is carried out via liquid-solid extraction [7,8] followed by quantification using infrared (IR) spectroscopy [4], gravimetry [3] or gas chromatography [9].

All of the methods applied at present are time-consuming and labor-intensive, and some produce environmentally harmful solvent waste of chlorofluorocarbons (CFCs). In 2000 [10], these CFC methods suffered another setback because per-halogenated solvents, such as carbon tetrachloride, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), tetrachloroethylene, etc., used for extracting TPHs from contaminated matrices were phased out, and local environmental protection agencies banned the use of CFCs [11,12]. As a replacement, n-hexane [5] and S-316 [13], di/trimers of chlorotrifluoroethylene, were approved. The solvent S-316 is very expensive, increasing the cost approximately

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fivefold per analysis. Also, n-hexane extraction requires a further preparatory step, the removal of n-hexane, before TPH quantification, which makes the procedure even lengthier and implies a partial loss of TPHs.

The above-mentioned constraints make it worthwhile to search for an alternative approach for determining TPHs – at least in soil, i.e., a method that is a solvent-free, rapid, and low-cost. Application of near-infrared reflectance spectroscopy (NIRS) in combination with principal component analysis (PCA) has shown that NIRS is a useful tool for analyzing soil properties [14–18]. Therefore, a study was undertaken to test the potential of NIRS for direct detection and quantification of TPHs in oil-contaminated soil. If reliable results were obtained, NIRS could be a valuable tool for identifying TPH-polluted land. Our investigations focused on soil contaminated with weathered crude oil (WCO) obtained from different locations in Kuwait's oil fields. Cleaned-up soil and the same soil spiked with TPHs ranging from gasoline to WCO served as reference samples. A chemometric method using OPUS-QUANT^{TM} software from Bruker was applied to a set of no. 43 reference samples to develop a model for predicting the TPH content between 0.1 and 5wt% in 26 field samples.

2 MATERIAL AND METHODS

A sieved sand with a particle size <2 mm (see Table 1) containing 6wt% clay, 4wt% slit and low moisture (<1wt%) obtained from southern Kuwait was cleaned by accelerated solvent extraction (ASE) using carbon tetrachloride (CCl_4) as a solvent [19]. Aliquots (40g) of this treated sand were spiked with different petroleum hydrocarbon mixtures such as gasoline, diesel, jet fuel, kerosene, atmospheric residue, Kuwait export crude oil, crude oil and WCO obtained from an aged oil spill in the desert (Table 2).

Two different soil spiking procedures have been applied depending on the volatility of the hydrocarbon mixtures. *Pentane preparation*: A 40g amount of dry and pre-cleaned soil was filled in a pre-cleaned 100m evaporation jar with wide-neck screw caps. For each spike the required mass of petroleum hydrocarbon (see Table 2) was swiftly injected into the jar, using a disposable 10ml syringe, while in place on the scale. The jar was promptly sealed after adding 15ml of n-pentane to the soil-TPH mixture. The spiked jars were left on the shaker for 24 hours at a 200-RPM cycle and then left to settle for another 24-hour period before uncapping inside a fume hood, where the pentane was allowed to evaporate at room temperature. Each jar required ten hours to have the pentane completely removed. Two pairs of control samples were processed along with the spiked samples: The first one contained dry soil. The second one contained the soil with the customary amount of 15ml of pentane. *Gasoline Spiking*: The soil spiking with gasoline simply consisted of mechanically shaking the gasoline/soil mixture in a properly sealed enclosure and allowing the vapors of the gasoline to diffuse throughout the soil over time, aided by a slight warming of the glassware. For this process, a set of pre-cleaned 500ml spherical flasks with matching stoppers were used. For the huge difference in masses between the added gasoline and the flasks filled with soil weighing the gasoline on

Table 1: Particle Size Distribution in Sieved Sand Samples.

	Particle Class				
	Very Coarse 1000-2000µ	Coarse 1000-500µ	Medium 500-250µ	Fine 250-100µ	Very Fine 100-53µ
%	8	8	22	39	23

Table 2: Set of Reference Samples Used for Developing a Regression Model.

TPH	No. of Samples	Concentration Range/wt%
Clean Soil[1]	4	0.00
Gasoline[2]	6	0.02–0.51
Diesel[3]	6	0.05–1.88
Jet Fuel[3]	6	0.04–1.43
Kerosene	6	0.04–1.33
Atmospheric Residue Oil[3]	4	0.39–2.19
Kuwait Export Crude[3]	3	0.50–1.93
Crude Oil[3]	7	0.02–1.36
Weathered Crude Oil (WCO)[3]	1	2.14

[1] Control samples from *Pentane preparation* procedures

[2] Spiked using the *Gasoline Spiking* procedure

[3] Spiked using the *Pentane preparation* procedure

the balance as performed in the previous procedure was impractical. The problem was solved by using a precision pipette (Witeg 25) for spiking. To a 200g amount of soil placed in a flask a measured amount of gasoline was added. Upon adding the gasoline each flask was promptly sealed with a glass stopper. The flask was shaken for 24-hours at 150 RPM. After shaking, the flasks were stored to allow for fumes of the gasoline within each sealed flask to diffuse through the enclosed soil.

The spiked TPH concentrations ranged from 0.02 to 2.19wt%. The spiked samples were re-extracted by ASE (average recovery of 44 individual hydrocarbon compounds: 99% [19]), and the TPH concentration of the CCl_4-extracts was determined by IR spectroscopy (RSD: 2.6% [4]) using calibration samples (TPH in CCl_4) made with the same contaminants used for spiking. The same spiked soil samples were analyzed by NIRS using an MPA^{TM} spectrometer from Bruker. The reflectance of each sample was measured three times in the range of 12,000–3,600 cm^{-1} (800–2,857 nm) with a resolution of 8 cm^{-1} and 32 scans. The spectra were converted into Kubelka-Munk [20] spectra. The final result was such that the quantity $(1\text{-}R^2)/2R$, where R is the ratio of the sample to the background reflectance (gold mirror), was linearly related to the concentration provided the scattering effects remained constant. Twenty-six TPH-contaminated field samples (soil + WCO) were each analyzed by both NIRS and conventional techniques (ASE followed by IR spectroscopy) to test the robustness and reliability of the chemometric model.

3 RESULTS AND DISCUSSION

3.1 Multivariate analysis

Based on a set of 4 control samples (not spiked) and 45 TPH-spiked samples with known and independently confirmed TPH contamination (using ASE followed by IR spectroscopy), a chemometric model was developed using OPUS-QUANT^{TM} software.

Briefly, the OPUS-QUANT^{TM} software [21] uses the partial last square (PLS 1) algorithm [22] to determine the property of a system, e.g., the TPH concentration in soil, from an experimentally observable, e.g., NIR spectrum. During PLS regression, the NIR spectra are reduced to only a few factors (loadings). The first loading shows the correlations between the the property of a system

(TPH concentration) and the spectral intensities of the calibration spectra. The following loadings will explain successively smaller parts until no further improvement is achieved. The PLS regression can be terminated if the property of a system is reproduced in a consistent way with the help of the loadings (regression). The number of PLS loadings used is defined in the OPUS-QUANT^{TM} program by the size of the 'rank'. Although PLS regression is a full spectrum method the removal of certain spectral ranges that do not contain valuable information can improve the predictive power of the model. Another important step while setting up the model is an appropriate data treatment of the spectroscopic information, especially for diffuse reflectance measurements of powdery samples [23]. The OPUS-QUANT^{TM} software supplies a routine that will automatically test combinations of varying spectral ranges and data treatment to optimize the prediction power of the model. Finally, the quality of the prediction model is validated by cross validation [24] (a leave–one–out validation). In case cross validation was chosen the OPUS-QUANT^{TM} program calculates the coefficient of determination (r^2) between true and predicted values and the root mean square error of cross validation (RMSECV) which can be taken as a criterion to judge the quality of the model.

TPHs, which basically comprise the entire class of petroleum hydrocarbons, consist mainly of CH_n-building blocks ($0 \leq n \geq 3$). Therefore, CH_2/CH_3-overtones and the CH_2/CH_3-combination bands of the C-H stretching vibrations are the most useful spectral signatures for use in correlating near-infrared (NIR) spectral information with TPH concentration. According to Chung et al. [25], there are two NIR regions where the most prominent spectral features of petroleum products are observed, 6,250–5,550 cm^{-1} (first overtone) and 9,090–6,650 cm^{-1} (second overtone). Due to the low concentration of TPHs (≤5%) the second overtone band was not observed in the contaminated field samples (Fig. 1).

Therefore, to develop a calibration model, two approaches were taken: (i) only the first CH_2/CH_3 overtone band (6,079–5,419 cm^{-1}) was chosen for calibration (model A, B), and (ii) calibration was

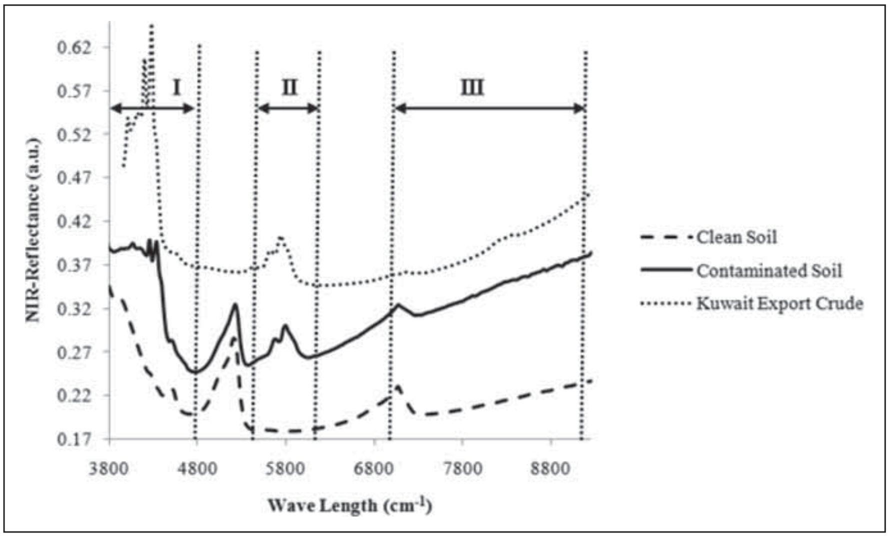

Figure 1: NIR-spectra (3,800–9,250 cm^{-1}) of clean soil (control sample from *pentane preparation* procedure), contaminated soil (5.15 wt% WCO) and Kuwait export crude – I: Combination region; II: First overtone region; III: Second overtone region.

Table 3: Calibration and Validation Statistics of the Regression Model Based on a Set of 43 Reference Samples.

Model	Spectral Range (cm^{-1})	Spectra Processing	RMSECV	r^2 Validation	r^2 Calibration	Rank	Bias
A	6383–5516	None	0.160	0.9400	0.9612	5	0.003
B	6383–5516	First Derivative	0.159	0.9406	0.9595	3	0.005
C	6079–5423 4478–4169	None	0.175	0.9287	0.9511	4	0.003
D	6079–5423 4478–4169	First Derivative	0.171	0.9320	0.9387	1	–0.002

carried out with two CH_2/CH_3 bands (model C, D), the first overtone band and the combination band (4,450–4,150 cm^{-1}). Although many NIRS studies on soil analysis favor the use of first-derivative spectra [26], we conducted the PLS regression with unprocessed (model A, C) as well as with first-derivative spectra (model B, D). The quality of each of the four regression models (A, B, C, D), i.e., two types of data processing combined with two different spectral signatures, was judged on the basis of two parameters, r^2 and RMSECV. Table 3 summarizes the calibration and validation statistics. There are only minor differences between the models, all of which predict the true TPH concentrations in the spiked test samples in a satisfactory manner.

3.2 Analysis of field samples

NIRS studies on soil properties have shown that reflectance spectra of soil are affected by moisture content and particle size distribution [27]. Therefore, the twenty-six field samples obtained from various oil fields in Kuwait and contaminated with WCO (0.1–5%) were selected under the condition that they have a similar texture and moisture content as the sand used as reference samples (spiked soil). The field samples were analyzed by NIRS and by conventional methods (ASE followed by IR spectroscopy). Figure 2 shows the predicted vs. true TPH contents (ASE + IR spectroscopy) for the field samples using the above-mentioned four regression models. Given the linear regression equations shown in the graphs, the standard deviations of the absolute differences between the true and predicted values for the four models are 0.251, 0.235, 0.242 and 0.236 (Table 4).

These results demonstrate that NIRS makes satisfactory predictions of the TPH contents in soil samples contaminated with WCO, and all four models are equal in prediction accuracy.

4 CONCLUSIONS

NIRS was used for the quantification of TPHs (weathered crude oil) in soil (0.5–5%). Using TPH-spiked samples, and applying partial last square (PLS 1) regression four models were develop for predicting the TPH content in field samples of soil. The same samples were analyzed by conventional methods (CCl_4-extraction followed by IR quantification). The correlation coefficient between the NIRS-predictions and conventional analyses was ≥0.928, with a the standard deviations of the absolute differences between the true (IR) and predicted (NIRS) values ≤0.251. This study shows that a solvent-free technique such as NIRS can be used as a fast, cost-effective, reliable and environmentally friendly analytical tool for screening TPH-contaminated soil.

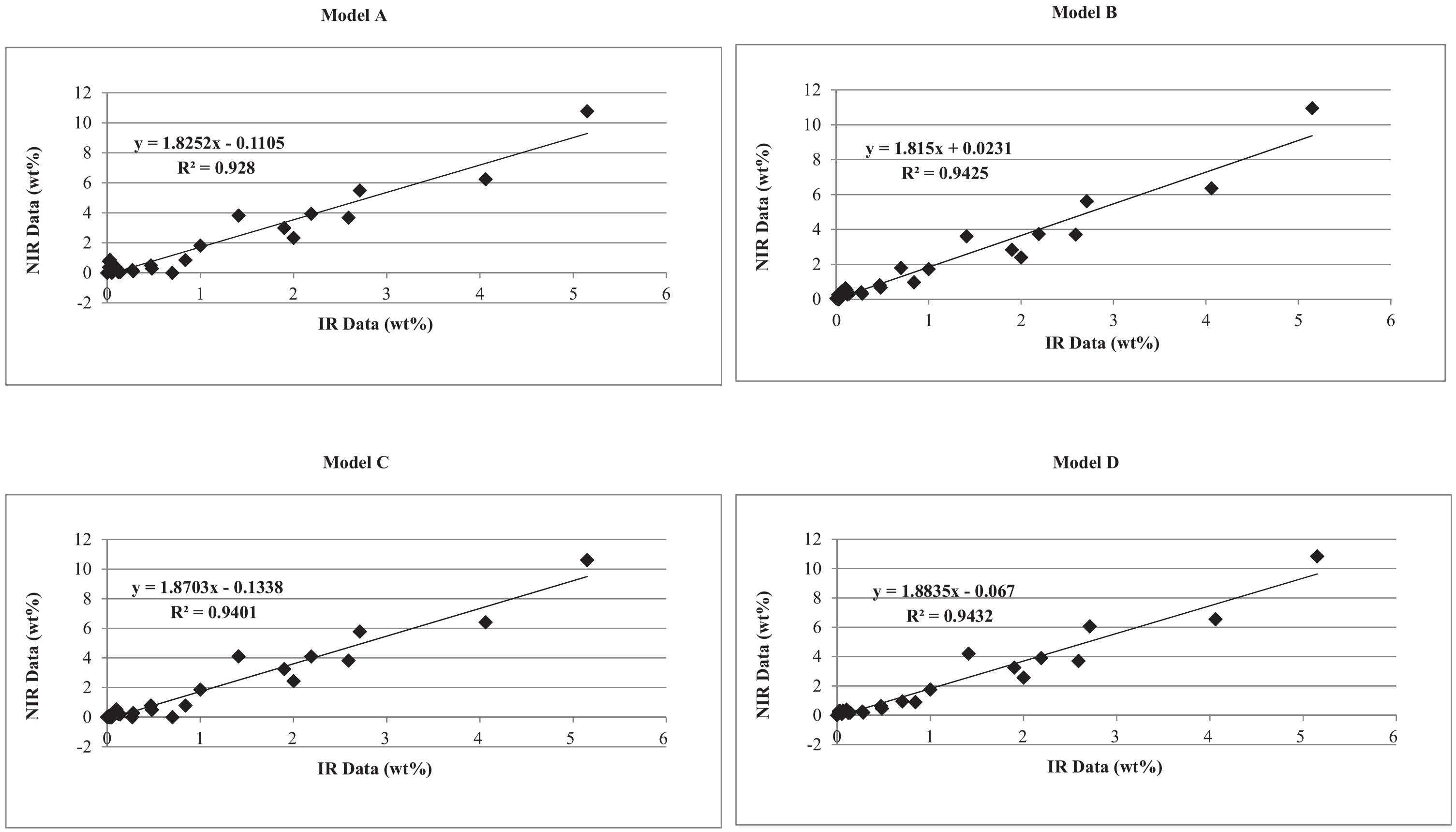

Figure 2: NIRS-predicted vs. true (ASE + IR spectroscopy) TPH content of field samples – A: (6383–5516 cm^{-1}) and no data processing; B: (6383–5516 cm^{-1}) and first- derivative spectra; C: (6079–5423 and 4478–4169 cm^{-1}) and no data processing; D: (6079–5423 and 4478–4169 cm^{-1}) and first-derivative spectra.

Table 4: True and Predicted TPH Values of 26 Contaminated Field Samples.

Sample No.	IR True TPH Value in wt%	NIRS Prediction in wt%			
		A	B	C	D
1	0.12	0.09	0.14	0.19	0.12
2	0.14	0.09	0.16	0.17	0.13
3	0.28	0.12	0.16	0.22	0.14
4	0.27	0.16	0.21	0.07	0.17
5	0.48	0.22	0.36	0.33	0.28
6	0.47	0.33	0.43	0.49	0.37
7	0.10	0.24	0.33	0.35	0.24
8	0.11	0.14	0.28	0.24	0.20
9	0.05	0.06	0.17	0.07	0.08
10	0.03	0.53	–0.01	0.07	0.19
11	0.02	0.48	–0.01	0.07	0.15
12	0.70	0.06	0.98	0.07	0.54
13	1.90	1.70	1.55	1.81	1.76
14	1.41	2.15	1.98	2.27	2.27
15	0.02	0.26	0.13	0.11	0.18
16	0.06	0.13	0.20	0.18	0.16
17	0.06	0.20	0.24	0.22	0.20
18	1.00	1.06	0.94	1.07	0.96
19	2.19	2.22	2.05	2.26	2.11
20	2.71	3.07	3.08	3.16	3.25
21	5.15	5.96	6.02	5.74	5.79
22	4.06	3.48	3.49	3.50	3.51
23	2.59	2.08	2.03	2.11	2.00
24	0.84	0.53	0.52	0.49	0.51
25	2.00	1.34	1.31	1.37	1.40
26	0.00	0.06	0.01	0.08	0.04
STDV[1]		0.251	0.235	0.242	0.236

[1] STDV: Standard deviation of absolute differences between true (IR) and predicted (NIRS) TPH concentrations.

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