An infrared spectroscopic test for total petroleum hydrocarbon (TPH) contamination in soils

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Abstract

The application of near- and mid-infrared (NIR and MIR) spectroscopy as a rapid screening tool for TPH concentrations in contaminated soils is presented. MIR-DRIFT (diffuse reflectance infrared Fourier-transform) spectroscopy, in particular, promises to be a revolutionary new technique for the in-situ analysis of soils at contaminated sites. Infrared is sensitive to alkyl vibrational frequencies, allowing the use of partial least squares (PLS) to be used for quantification of TPH. This work showed that neat whole soils could be used, spectra can be acquired rapidly, and MIR TPH spectra could be separated from those of natural soil organic matter. PLS regression analyses were carried out in three stages; spiking diesel and crude oil (as TPH) into reference minerals, spiking into reference soils, and actual TPH concentrations in contaminated soils. Results of PLS cross-validation for the spiked minerals showed that prediction errors (RMSECV) with the MIR DRIFT were approximately 2000-4000 mg/kg for a TPH range of 0-100,000 mg/kg, but slightly higher for the NIR. (4500-8000 mg/kg). RMSECV values for the reference soils were approximately 1500-2500 mg/kg for a 0-25,000 mg/kg TPH range. Tests with actual contaminated soils identified specific peaks in the MIR that were characteristic of TPH, and showed that predictions using these peaks resulted in RMSECV of approximately 4,500 mg/kg for a 0-60,000 mg/kg TPH range and thus suitable for use as a screening tool.

Key Words

TPH, PLS, infrared, soils, DRIFT.

Introduction

Currently, most soil analyses for TPH use a gas-chromatographic (GC) based laboratory method for determining TPH concentration. Although this method is the industry standard, as required by state regulatory agencies, it is time-consuming, requires a NATA accredited laboratory, and is not suited to field-portable or on-site applications. A more simple and rapid alternative method for screening contaminated sites for TPH would be desirable, even if slightly less accurate, for initial TPH screening of samples at contaminated sites.

Infrared (IR) techniques may satisfy these requirements, particularly with the availability of portable spectrometers. A literature search resulted in very few studies on the use of IR for TPH determination in soils, and in particular using unprocessed neat whole soils (Malley *et al.* 1999). Currently, a quantitative assessment of TPH can be carried out with an ATR (attenuated total reflection) infrared technique following solvent extraction of TPH from the soil sample. However, the extraction method is somewhat tedious to carry out in the field and, due to the extraction step, is not rapid nor lends itself to in-field application as a direct measurement method. This work outlines the scientific basis, methodologies and the results for the prediction of TPH concentrations in contaminated soils using Fourier transform infrared (FTIR) spectroscopy and partial least squares (PLS) regression on neat whole soils. The results demonstrate the potential of mid-infrared DRIFT spectroscopy for TPH using laboratory based and field portable spectrometers.

Near-infrared (NIR) and mid-infrared (MIR) spectra are sensitive to alkyl functional chemical groups in organic materials, including TPH compounds. These techniques therefore have the possibility of screening contaminated soils to determine TPH contamination. An advantage of IR methods is that un-processed neat, whole soil samples can be studied by diffuse reflectance infrared (DRIFT) spectroscopy, where the samples are simply put under an incoming infrared beam and the reflected signal analysed. However, there are inherent problems with the application of the DRIFT technique to whole soil analysis of TPH. The first problem is the overlap of TPH-sensitive infrared peaks with those of naturally occurring soil organic matter (SOM), so that identification of spectral peaks unique to TPH is difficult. Adding to this problem is masking of many of the TPH peaks in the MIR in spectral regions dominated by quartz and other soil mineral spectra.

A second known problem with infrared reflectance is the shielding to IR radiation to the internal structure of soil micro-aggregates. This study attempts to address some of these problems and develop a rapid *in-situ* screening technique for TPH contamination of soils.

The project was carried out in three stages. The first stage dealt with the sorption of diesel and crude oil (representing TPH) into some common soil clay minerals (illite, smectite, kaolinite), sand, mixtures of clay and sand, and a range of quartz particle sizes. The second and third stages focused on TPH sorption into two standard reference soils, and on a wider range of field soils from actual TPH contaminated sites. Various spectrometer options, including dispersive and FTIR instrumentation, were available for alternative NIR and MIR spectral ranges and sample presentations. It was thus hoped to demonstrate that infrared spectroscopy could be used to speed up routine TPH analysis, allowing for more timely management decisions to be made with regard to site contamination and remediation, with a potential for future in-field or on-site application.

Methods

Samples

Crude oil and diesel at various concentrations were spiked into reference soil minerals and soils and analysed using FTIR and NIR reflectance with PLS regression. Minerals used were sand, bentonite, kaolinite, illite and limestone. Stock solutions of TPH were prepared from crude oil and diesel dissolved in cyclohexane. The aliquots were mixed with fixed weights of each sample in a tumbler to ensure an even dispersion of TPH throughout the sample particles and then the samples were dried to remove the cyclohexane. Loss of TPH resulted in only 2% in 24 hrs. Two sets of “real” contaminated soils were tested; set “S” consisting of 34 soils and set “L” consisting of 138 samples. Most of the TPH as analysed by the primary laboratory method was found in the C15-C28 carbon length fraction.

Spectroscopy

MIR DRIFT spectra were scanned using approximately 100 mg of soil with a *Perkin-Elmer Spectrum-One* Fourier transform mid-infrared (FTIR) spectrometer (Perkin Elmer Inc., Mass. USA). Spectra were scanned for 60 seconds in the frequency (wavenumber) range 7800 to 450 /cm (wavelength range 1280 to 22000 nm) at a resolution of 8 /cm. Reference scans of liquid crude oil and diesel were also obtained by two reflectance methods; as films deposited directly onto a mirror surface (transflectance) and dispersed on the surface of powdered KBr (DRIFT). NIR spectra were scanned using a FOSS *NIRSystems 6500* Vis-NIR spectrometer (Foss NIRSystems, Silver Springs, MD, USA) with a wavelength range of 400 – 2500 nm. Samples for NIR were placed “as received” into a quartz macro-sampling cuvette with an area of approximately 200x25 mm and scanned in reflectance mode. Reference scans of crude oil and diesel were carried out by transmittance using a 1 mm quartz cuvette. Portable NIR and MIR spectrometers were also tested.

PLS chemometrics

Spectra were processed with the Unscrambler™ Ver. 9.60 software (CAMO technologies, Inc, 152 Woodbridge, NJ). Principal components analysis (PCA) and PLS calibrations were carried out using full "leave-one-out" cross-validation (Geladi and Kowalski 1986). Cross-validation regression statistics were expressed in terms of the coefficient of determination (R^2) and root mean square error of cross-validation (RMSECV). The detection limit was taken as 2.0 x RMSECV.

Results and discussion

Peaks characteristic of alkyl–CH_3 and –CH_2 stretching vibrations were observed in the ranges 4500-4200 /cm and 3000-2700 /cm. Of the various alkyl absorbance peaks, one was observed and attributed to the first overtone vibration of the –CH_3 symmetric deformation mode in TPH but this peak was not observed in the spectra of soil organic matter SOM. These seemed to be related to the amount of diesel in the spiked samples rather than to SOM.

As shown by Figure 1 there was a strong influence of sample porosity on IR signal intensity, with porous clay minerals resulting in much weaker signals compared to non-porous sand. This was attributed to shielding of the TPH within internal soil structures to the IR beam. A dramatic signal reduction, by up to a factor of 100 could be observed by mixing clay with sand at a proportion of up to 25% clay. It appears therefore that even a minor amount of clay can seriously reduce the apparent intensity of sorbed TPH spectral signals.

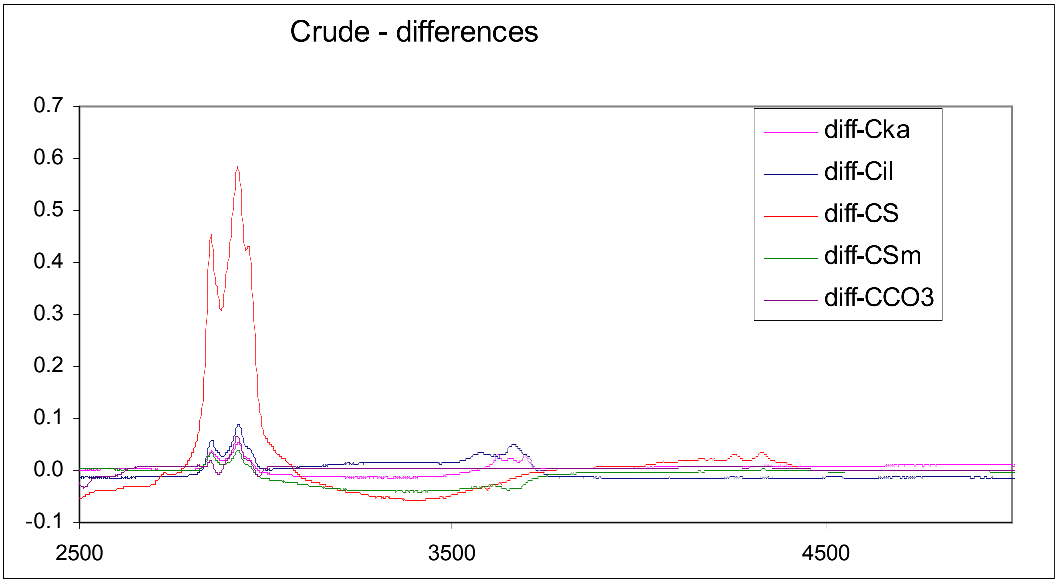

Figure 1 DRIFT spectra of crude oil adsorbed onto soil minerals from a 1% solution of crude in cyclohexane. (diff-Cka) kaolinite, (diff-Cil) illite, (diff-CS) sand, (diff-Sm) smectite, (diff-CCO3) carbonate. Crude oil spectra were derived by difference between spiked mineral spectra and raw minerals.

PLS cross-validation results for crude oil spiked into soil minerals are shown in Table 1. Prediction errors (RMSECV) ranged from 700 to 4,200 mg/kg, depending on the range of crude oil in the PLS models. Errors were higher for the NIR portion of the FTIR spectra, although the NIRS6500 gave better results for sand and smectite.

Table 1. PLS cross-validation prediction of TPH in reference minerals. Standard errors (RMSECV) are shown in parentheses.

Mineral	Crude oil (mg/kg)	FTIR (MIR) (RMSECV mg/kg)	FTIR (NIR) (RMSECV mg/kg)	NIRS6500 (RMSECV mg/kg)
Kaolinite	0-10,000	700		
Illite	0-10,000	1900		
Smectite	0-100,000	2400	6300	2600
Carbonate	0-100,000	4200	4500	
Quartz	0-100,000	3900	8000	3000

Results for the reference standard soils were also considered to be reasonable, with RMSECV values ranging from approximately 2,500 ppm in the 0-25,000 ppm range (REF1) to 1,700 ppm in the 0-10,000 ppm range. Similar results were obtained for the FT-NIR. Cross-validation errors were therefore approximately 10% of the range of TPH in the calibration sets.

During the course of studies a number of very weak spectral peaks, apparently unique to TPH, were detected in the MIR –CH stretching frequency range. These peaks were attributed to combination and overtone vibrational frequencies of terminal methyl (-CH_3) chemical groups found in higher proportion in diesel and crude oil than in the longer chain length soil organic matter, and thus important for the accurate determination of TPH in a wide range of soils in the presence of SOM. Prediction accuracy appeared to be enhanced when these signatures were used, since they could be used to separate the IR signals for short-chain terminal –CH_3 groups in diesel and crude oil from those of long-chain hydrocarbons in the native SOM.

Results for the field soils were less satisfactory, with cross-validation reasonably accurate for the “S” set but worse for the “L” set. This was attributed to a number of factors, including mismatch between sub-samples used for reference laboratory analysis and those analysed by IR and very high sample inter- and intra-aggregate variability in the “L” set. Total TPH concentrations were predicted from a subset of the “L” soils ranging up to 60,000 ppm (see Figure 2) with an RMSECV=4,653 mg/kg.

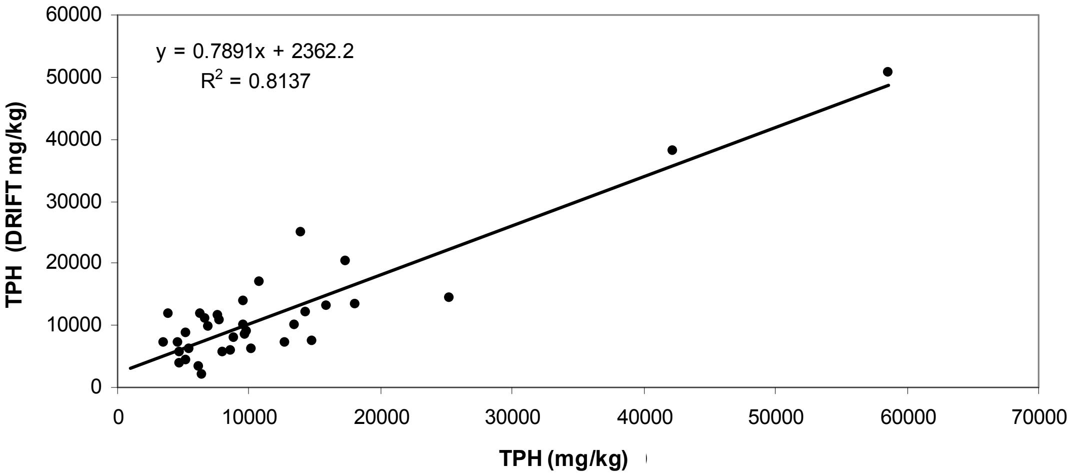

Figure 2. FT-MIR PLS calibration for total TPH derived from 35 "L" samples.

Conclusions

It was concluded from this preliminary study that the MIR DRIFT method could satisfy the required accuracy requirements for field screening, provided that certain experimental conditions could be met; the *same* sub-sample must be used for each training/validation IR and laboratory measurement as far as possible, the peaks used to build the IR calibration models use the most effective spectral signatures, and minimal TPH is lost between receipt of samples and sample scanning, the predicted TPH values for field screening are offset or normalised by a few reference laboratory control data, and surface area, particle size and surface effects are taken into account. An encouraging finding of this study was the possibility of being able to discriminate between TPH and SOM which current techniques are unable to do. This study suggests that, with recent availability of truly field portable MIR spectrometers, the in-situ measurement of contaminants in soils has become more feasible.

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