



Quantitative characterization of crude oils and fuels in mineral substrates using reflectance spectroscopy: Implications for remote sensing



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ABSTRACT

The near and shortwave infrared spectral reflectance properties of several mineral substrates impregnated with crude oils (\circ APIs 19.2, 27.5 and 43.2), diesel, gasoline and ethanol were measured and assembled in a spectral library. These data were examined using Principal Component Analysis (PCA) and Partial Least Squares (PLS) Regression. Unique and characteristic absorption features were identified in the mixtures, besides variations of the spectral signatures related to the compositional difference of the crude oils and fuels. These features were used for qualitative and quantitative determination of the contaminant impregnated in the substrates. Specific wavelengths, where key absorption bands occur, were used for the individual characterization of oils and fuels. The intensity of these features can be correlated to the abundance of the contaminant in the mixtures. Grain size and composition of the impregnated substrate directly influence the variation of the spectral signatures. PCA models applied to the spectral library proved able to differentiate the type and density of the hydrocarbons. The calibration models generated by PLS are robust, of high quality and can also be used to predict the concentration of oils and fuels in mixtures with mineral substrates. Such data and models are employable as a reference for classifying unknown samples of contaminated substrates. The results of this study have important implications for onshore exploration and environmental monitoring of oil and fuels leaks using proximal and far range multispectral, hyperspectral and ultra-spectral remote sensing.

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1. Introduction

The occurrence of natural seepage in continental areas is a subject not openly explored, despite its importance. Early identification of natural crude oil occurrences can be used to guide oil exploration, since the presence of petroleum hydrocarbons (PHCs) on the surface represents the end of the migration path. Although not definitive indicators of economically feasible areas for exploration, natural seepages indicate the presence of some type of oil reservoir in subsurface.

The extraction, refinement and transportation of petroleum pose innumerable chances of spillage, which can cause significant damages to the environment. In addition to the contamination problem in isolated locations (e.g. refineries, oil fields), contam-

ination can also occur in wildlife refuges and national parks, endangering ecosystems (Fine et al., 1997). Knowledge about the concentration and nature of the oil are vital to track their propagation in the environment, to assess risks and to propose remediation strategies (Okparanma and Mouazen, 2013b).

The small scale of onshore oil shows and the complex interaction with soils hinders the detection of oil at the surface. Besides, the similarity between soils impregnated with crude oils and fuels and soils with high moisture content also challenge the visual identification of contaminated sites (Fig. 1). Traditional methods employed to define the origin and concentration of petroleum products in soil samples involves the extraction of the contaminant from the soil, followed by its determination using gas chromatography with flame-ionization or mass spectrometry detection, general gravimetry, immunoassay and spectroscopic techniques (e.g. Raman, fluorescence) (Dent and Young, 1981; Schwartz et al., 2012; Okparanma and Mouazen, 2013a). Most of these analytical techniques are expensive, involve time-consuming sample preparation protocols and rely on the use of noxious extraction

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Fig. 1. Helicopter view (VIS camera) of breached oil containers near New Orleans (USA) after the hurricane Katrina episode, in August 2005. Note that is ambiguous the interpretation about the nature of the dark material around the tanks, which may be either water, oil or a mixture of both (source: U.S. Environmental Protection Agency—<http://archive.epa.gov/katrina/web/html/photogallery.html>).

solvents that tend to pose health risk to operators (Okparanma and Mouazen, 2013b).

Infrared (IR) spectroscopy has been recognized as a reliable alternative method for direct detection of PHCs (Cloutis, 1989; Lammoglia and Souza Filho, 2011). Despite not being the most usual method for this purpose, IR spectroscopy has also proved to be a simple, fast and cost-effective method for rapid detection and characterization of PHC-contaminated soils (Forrester et al., 2010; Schwartz and Ben-Dor, 2011; van der Meijde et al., 2012; Chakraborty et al., 2012, 2014; Okparanma and Mouazen, 2013c; Okparanma et al., 2014).

More specifically, near and shortwave infrared spectroscopy (NIR-SWIR; 700–3000 nm) is presently a popular method for quick identification and quantification of PHCs in contaminated soils, with reasonable levels of accuracy, specially due to the portability of the devices and minimum or no preparation and pre-treatments required for the samples (Graham, 1998; Malley et al., 1999; Forrester et al., 2010; Chakraborty et al., 2010, 2014; Schwartz et al., 2012; Ben-Dor and Schwartz, 2013). Moreover, NIR-SWIR spectra provide useful information on organic and inorganic materials in soil (Viscarra Rossel et al., 2006; Vasques et al., 2009; Stenberg, 2010). Crude oils and petroleum fuels (i.e. diesel, gasoline) have diagnostic absorption bands centered around 1725 nm and 2310 nm (Cloutis 1989; Winkelmann, 2005; Lammoglia and Souza Filho, 2011; Okparanma and Mouazen, 2013c). Therefore, the spectral information gathered in the NIR-SWIR range is excellent for both qualitative and quantitative analysis of PHC-contaminated soils (Chakraborty et al., 2014).

The origin of NIR-SWIR absorption bands of crude oils and fuels is attributed to primary combinations and overtones of C–H stretching modes of saturated CH₂ and terminal CH₃, or aromatic C–H functional groups (Aske et al., 2001). However, the broad bands resulting from the overtones hinder the quantitative interpretation of the spectra. The use of multivariate techniques can overcome this problem by using the intensity and wavelength positions of the vibrating molecule to identify the properties of the substance (de Jong, 1993; Davis, 2002; Geladi, 2003; Pasquini, 2003; Abdi, 2007). When analyzing spectroscopic data, multivariate calibration generally solves the problem of interference from compounds closely related to the target, thereby eliminating the need for selectivity (Okparanma and Mouazen, 2013b).

Table 1
Mineral substrates and contaminants used in the experiment.

NOMENCLATURE	CONTAMINANT	NOMENCLATURE
SAND	CRUDE OIL °API 19.2	O1
LAT	CRUDE OIL °API 27.5	O2
GIB	CRUDE OIL °API 43.2	O3
DOL	DIESEL	DIS
KAO	GAS	GAS
MONT	ETHANOL	ETN

Currently, there is only limited literature on application and accuracy of this methodology to predict petroleum compounds in soils using NIR-SWIR data. Some authors have used regression techniques, coupled with spectral preprocessing, in order to generate statistical models to identify and differentiate petroleum PHC products in mixtures with mineral substrates (Stallard, 1996; Zwanziger and Förste, 1998; Hidajat and Chong, 2000; Chung et al., 1999; Falla et al., 2006; Schwartz et al., 2009; Forrester et al., 2010; Lyder et al., 2010; Rivard et al., 2010; Zhaoxia et al., 2011; Okparanma and Mouazen, 2013b; Chakraborty et al., 2014). However, the accuracy and application of such models is challenging, because they have been developed for specific or local soil types, boosting false positives and restricting a global application (Schwartz et al., 2012).

In this context, the aim of this study is to create a reference spectral library of impregnated soils and predictive models using a controlled contamination experiment, involving several mineral substrates with various types and concentrations of crude oils and fuels in order to achieve two main goals: (i) to characterize the absorption features of PHCs-fuels in spectra yielded from contaminated soils, establishing detection limits, as well as waveform parameters that can be used to effectively identify and classify contaminated sites based on NIR-SWIR spectra; and (ii) to create predictive models for detection of several mineral substrates impregnated with PHCs-fuels that could be applied worldwide to both oil exploration and environmental monitoring and remediation.

2. Methods

2.1. Sample preparation

Two groups of samples were used in this study: contaminant samples (Group I) and mineral substrates samples (Group II). Group I is composed of three samples of crude oils provided by Petrobras with °APIs of 19.2; 27.5 and 43.2, plus diesel, gasoline and ethanol. Group II comprises six samples of mineral substrates (MS): clayey soil rich in kaolinite, clayey soil rich in montmorillonite, dolomitic soil, sandy soil rich in quartz, latosol and lateritic soil rich in gibbsite (Table 1). Soil samples vary in grain size. Clayey and dolomitic soils have fine and homogeneous grains. Sandy soil, lateritic soil and latosol are heterogeneous, with grain size varying from medium to coarse.

Thirty-six (36) combinations were prepared in this experiment by mixing each mineral substrate with various concentrations of each contaminant in a Petri dish (60 mm of diameter). For the preparation of each combination, 10 m³ of a specific mineral substrate were added to the dish followed by the addition of 0.1 ml of a specific contaminant to the same dish, using a syringe. A disposable plastic spoon was used to homogenize the mixture, after which a reflectance measurement was taken by a high resolution spectrometer (three measurements were taken for each mixing stage). Next, the same soil-contaminant combination (i.e. the same Petri dish) received an additional 0.1 ml of contaminant, which was once again homogenized and measured with the spectrometer. This scheme was repeated until the dish reached a concentration of 0.5 ml of contaminant. The same process was repeated adding 0.5 ml of the

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