

# Spectral Library for Oil Types

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**Abstract - Oil spill events are a crucial environmental issue. Although they are adequately detected using SAR images, there is a weakness regarding oil type and thickness detection. Thus, potentials of hyperspectral methods in this field are also investigated. Towards this direction, spectral signatures of different oil types for various thicknesses and in various time intervals are very useful, since they may serve as endmembers in unmixing and classification models. This paper describes the development of a relevant spectral library using spectral measurements with a GER1500 spectroradiometer. Results showed that spectral signatures of different oils types present distinctive characteristics through the whole spectral region. These characteristics are useful for oil type discrimination. Relatively high correlation has been observed between the reflectance values and the oil spill thickness, as well as the age of the oil spills. Consequently, best-fit functions, which effectively express the relationship between the reflectance and oil spill thickness as well as the age of the oil spills, have been calculated. According to these results, there is high potential of using hyperspectral imagery in order to estimate oil spill features adequately.**

**Keywords:** radiometric measurements, oil spills, spectral library, thickness, age.

## 1. INTRODUCTION

Detection of oil spills is important for both oil exploration and environmental protection. The determination of the pollutant type as well as its thickness and its weathering state is crucial for the cleanup crews in order to identify the best cleanup method, the environmental impacts and the modeling techniques (to predict the flow path, dispersion rate etc), (Salem and Kafatos, 2001). Also, determination of the oil type could contribute to the identification of the ship-vessel that is responsible for the pollution. Petroleum products most likely to be released into the marine environment are crude oils, bunker C, fuel oils and light petroleum products (Wilson and Hunt, 1975). There have been several studies concerning the oil spills. More specifically, Salisbury et al., (1993) examine the spectra effects of slick thickness, age and composition in the thermal infrared region and conclude that there is a uniform spectra background, against which oil slicks can be detected. Palmer et al., (1994) analysed an oil spill event with Compact Airborne Spectrographic Imager (CASI) and concluded that the spectrum from 440 to 900 nm is effective for detecting the marine oil spill. Zhao and Cong, (2000) drew the conclusion that reflectance of various kinds of offshore oil slicks present peaks in the spectral regions from 500 to 580 nm. Salem, (2003) demonstrated that the increase of oil quantity causes light absorption to increase, and thus the reflectance in the visible bands is reduced. The near infrared electromagnetic spectrum from 600 to 900 nm provides the greatest possibility for oil slick detection using remote sensing techniques.

Svejkovsky and Muskat, (2006) and Svejkovsky et al., (2008) present a real time method to estimate the oil slick thickness of crude oils and fuel oils using multispectral sensor. The proposed algorithm showed that oil thickness distributions up to 200-300 $\mu$ m can be mapped with accuracies of 70%. However, for oil films thicker than approximately 50 $\mu$ m the approximate oil type must be known or estimated for the algorithm. YingCheng1 et al., (2008) studied the change of reflectance spectrum of artificial offshore crude oil slick with its thickness and concluded that spectral characteristics of oil spills are very distinct at 550 and 645 nm.

Previous researches focused on analyzing spectral characteristics of oil spills regardless the oil type and its weathering state. In this paper, spectral signatures of a wide variety of different types of oil were gathered. Spectroradiometer data acquired from laboratory experiments are used to provide high quality spectral measurements for a) developing a spectral library for different oil types, b) testing their behavior and defining the weathering state of a floating oil slick over time, c) defining the oil slick thickness. Exploitation of the results of these experiments will improve the performance of classification algorithms of remote sensing hyperspectral imagery.

## 2. EXPERIMENTAL METHOD

### 2.1 Ancillary Data

Samples for 13 different oil types were collected from two Greek refineries: Hellenic Petroleum (ELPE) S.A. and Motor Oil Hellas S.A.. 7 of them were crude oils, 1 was heavy fuel oil, 3 were marine residual fuel oils and 2 were light petroleum products (Table 1). The sample oil types were classified as light, medium or heavy, according to their density. Light oil is the petroleum that has a low density and flows freely at room temperature. It also has a low viscosity and low specific density (gravity) due to the presence of a high proportion of light hydrocarbon fractions.

Table 1. Samples which were used for laboratory experiments

TYPE OF OIL	NAME OF OIL	DENSITY (kg / l)
CRUDE OILS	CPC BLEND – (Russia)	0.8042 – (light)
	SARIR – (Libya)	0.8396 – (light)
	ARABIAN EXTRA LIGHT – (Saudi Arabian)	0.8345 – (light)
	REBCO – (Russia)	0.8701 – (medium)
	PRINOS – (Greece)	0.8656 – (medium)
	KIRKUK – (Iraq)	0.8447 – (medium)
	SIBERIAN – (Siberia)	0.8358 – (light)
HEAVY FUEL OIL	SRFO	0.975 – (heavy)
MARINE RESIDUAL FUEL OILS	RME 180	0.9902 – (heavy)
	RMG 380	0.9902 – (heavy)
	BUNKER 3	0.9950 – (heavy)
LIGHT PETROLEUM PRODUCTS	HEATING OIL	0.8397 – (light)
	KEROSENE	0.8024 – (light)

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On the contrary, medium oil or heavy oil is any type of petroleum which does not flow easily. Medium oil is defined as having density between 0.87 to 0.93 kg / l. Heavy oil has been defined as any liquid petroleum with a specific gravity greater than 0.933. The latter mostly results from oils getting degraded by being exposed to bacteria, water or air, resulting in the loss of its lighter fractions while leaving behind its heavier fractions (Dusseault, 2001). As it is observed in Table 1 the samples show a wide range of density values.

## 2.2 Laboratory tests

Spectral data were acquired with the GER1500 spectroradiometer. The spectroradiometer has a spectral range between 280nm-1093nm (visible and near infrared). The instrument acquires 512 bands. Laboratory experiments included measurements of the spectral signature of oil samples at different time intervals and for various oil slick thicknesses. Preliminary experiments took place using different vessels in order to test several reflecting backgrounds (white, black, grey) and the most appropriate vessel depth. Results showed that black background was more appropriate because it simulates sea background and constrains reflectance. After several experiments, vessels with a height of 0.7 m have been selected in order to constrain illumination variability and to approximate real-world conditions of deep water. During the preliminary experiments, several oil slick thicknesses have been tested and it was observed that at thicknesses greater than 200µm reflectance of the oil film characteristic does not change significantly. This occurs since at these thicknesses sunlight no longer penetrates through the entire film (Svejkovsky and Muskat, 2006). Thus, six different oil film thicknesses of 1µm, 5µm, 10µm, 50µm, 100µm and 200µm were selected for the final experiments.

Measurements over time were implemented for the oil slick thickness layer of 200µm. Spectral measurements for the 13 samples (Table 1) and the pure water took place under constant sunny conditions. The measurements of the weathering state of the floating oil lasted 5 days and were repeated every day at 12.30pm.

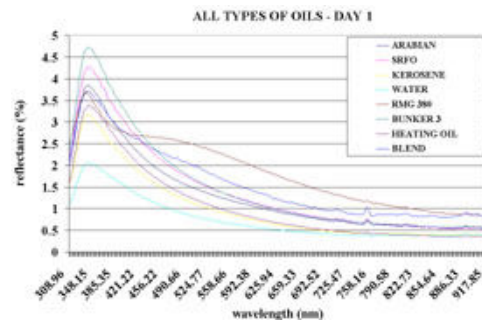
## 2.3 Experimental Results

The spectroradiometer experiments led to constructive results. Graphs 1(a)-1(e) present the spectral signatures of all the oil types during time at thickness of 200 µm. For simplicity reasons, Arabian crude oil was selected as the most representative among crude oils. As for the marine residuals, RMG 380 and Bunker 3 were selected for demonstration as they present some differences in their spectral signatures. Spectral signature of RME 180 resembles RMG 380. It should be noted that the ranges 280 nm - 307 nm and 920 nm - 1093 nm were excluded due to noise effects. Observation of the graphs shows that:

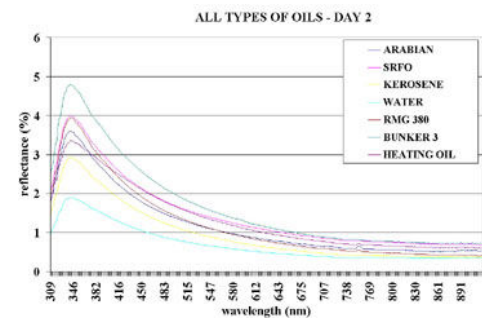
- The slope of the spectral signature of Blend crude oil differs from the other samples.
- The slope of the heating oil spectral signature differs from the other signatures from the second to the fifth day.
- Concerning marine residuals fuel oils (RME 180, RMG 380, Bunker 3), due to their high viscosity, dark spots appear producing different spectral signature from all the other oil types during the first day.
- Reflectance is rising from light to heavy oils at the spectral range of 308.96 nm – 367.84 nm for the whole duration of the experiments. Only RMG 380, whose signature results from spots with different thicknesses, has different behaviour. For the rest of the oil types the

reflectance values are ordered as follows:  $R_{\text{WATER}} < R_{\text{KEROSENE}} < R_{\text{HEATING OIL}} < R_{\text{CRUDE OIL}} < R_{\text{HEAVY FUEL}} < R_{\text{MARINE FUEL OIL}}$ .

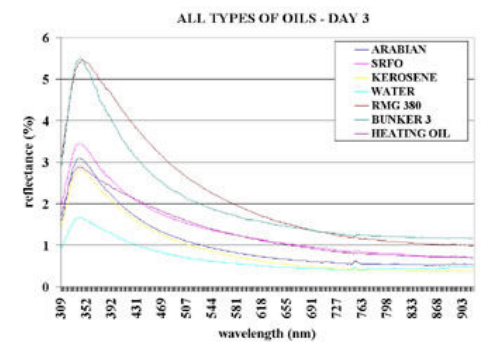
As it is observed in graphs 1(a)-1(e), in a region around 344.51 nm the spectral signatures present a peak. The greater differences in reflectance values are also observed around this wavelength. This region of wavelength provides significant conclusions concerning the spectral signatures of oil types in comparison to the spectral signature of the pure water.



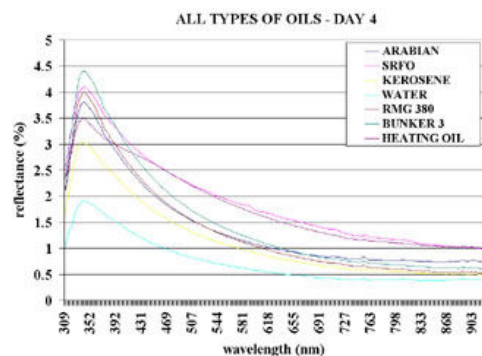
(a)



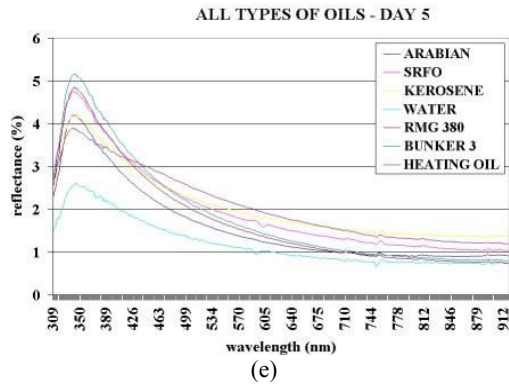
(b)



(c)



(d)



Graph 1. Spectral signatures of all types of oil at (a) the first day, (b) the second day, (c) the third day, (d) the fourth day, (e) the fifth day.

More specifically a) crude oils (apart from SARIR) present similar spectral signature behaviour with water over time. Their variation focuses on the values of reflectance, since those of water's are lower, b) spectral signatures of all the marine residuals fuel oils (RME 180, RMG 380, Bunker 3) have different slopes than those of water especially the third day.

In addition, in this particular wavelength, ratios between reflectance of each oil type and reflectance of pure water were computed for each day. Studying these signature ratios showed that although the order  $R_{\text{WATER}} < R_{\text{KEROSENE}} < R_{\text{HEATING OIL}} < R_{\text{CRUDE OIL}} < R_{\text{HEAVY FUEL}} < R_{\text{MARINE FUEL OIL}}$  is preserved for 5 days, the ratios are constant for the first two days regarding to Kerosene, Heating oil and Bunker 3, and for the first three days regarding to crude oils and SRFO. This was expected as by the time oil enters the marine habit it undergoes to several physical and chemical reactions which become more intensive as time passes. These reactions reduce the concentrations of hydrocarbons in sediment and water and alter the chemical composition of oil spills (Clark, 2001). Consequently, identification of oil type can be achieved if data are selected within the first 72 hours after the oil spill event. Table 2 presents the ratios between reflectance of each oil type and reflectance of pure water at 344.51 nm. At this wavelength corresponding ratios between reflectance of unknown oil and pure water in the image should be calculated in order to identify the type of oil.

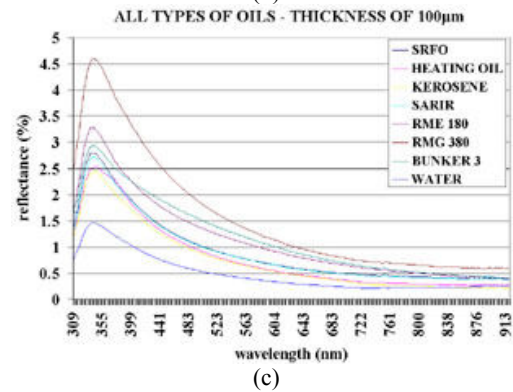
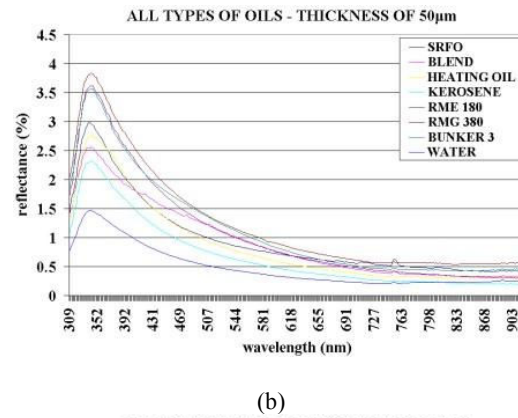
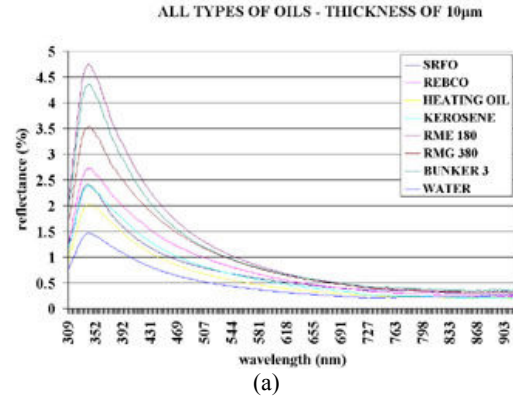
Table 2. Ratios between reflectance of each oil type and reflectance of pure water

OIL TYPE	RATIOS	DAYS
KEROSENE	1.53-1.54	1,2
HEATING OIL	1.64-1.76	1,2
CRUDE OIL	1.86-1.89	1,2,3
SRFO	2.08-2.09	1,2,3
BUNKER 3	2.30-2.51	1,2

Graphs 2(a)-2(c) present the spectral signatures of samples which vary in oil thickness. The conclusions of the spectral signatures behaviour are the following:

- Marine residuals fuel oils present the greatest values and increase of reflectance in comparison to the others. They have similarities with specific crude oils. Probably they are generated from them, but verification of this assumption is required.

- The order  $R_{\text{WATER}} < R_{\text{KEROSENE}} < R_{\text{HEATING OIL}} < R_{\text{CRUDE OIL}} < R_{\text{HEAVY FUEL}} < R_{\text{MARINE FUEL OIL}}$  in the reflectance values exists for layers of 50µm and above.
- No specific or unique reflectance/absorbance peak exists at any wavelength that distinctly changes with oil thickness.



Graph 2. Spectral signatures of oil types at thickness of (a) 10µm, (b) 50µm, (c) 100µm

#### 2.4 Estimation of thickness and age of oil spills

Correlation analysis between the reflectance values at all the wavelength ranges (bands) and the oil spill thicknesses was carried out. Results were very interesting as it is observed that a) each type of oil (crude oil, heavy fuel oil, light petroleum products) presents a different wavelength region in which reflectance values and oil thicknesses are correlated (see table 2), b) marine fuel oil signatures are uncorrelated to thickness, probably due to their high viscosity and difficulty to spread in the water.

Table 3 presents the results of the correlation analysis. Firstly, the wavelength region which presents high correlation values between reflectance and oil slick thickness has been selected. These wavelength regions are different for each oil type. It should be noted that Prinos and Siberian crude oils, present correlation values below 0.6, thus they were excluded from further analysis. Secondly, exponential and polynomial best-fit functions for each oil type were calculated according to the values of reflectance at each oil thickness. By observing the coefficients of determination (R-squared values) it is obvious that these best-fit functions can be used sufficiently in order to estimate oil slick thickness. As shown in table 3, oil thickness in  $\mu\text{m}$  is given by  $y$  when  $x$  is the average value of reflectance within the corresponding wavelength region for each oil type.

Table 3. Estimation of oil slick thickness

NAME	WAVELENGTH (nm)	VALUE OF CORRELATION	EQUATION	R <sup>2</sup>
HEAVY FUEL OIL	893.85-917.85	0.61	$y = 0.0027e^{25.204x}$	0.94
HEATING OIL	474.31-500.44	0.81	$y = 991.56x^2 - 1512.1x + 582.19$	0.88
KEROSENE	839.47-863.71	0.70	$y = 2E-05e^{66.579x}$	0.86
CRUDE OIL	714.52-739.51	0.79	$y = 6650.8x^2 - 4238.3x + 675.46$	0.98

Similarly to this, correlation values between the reflectance values at all the wavelength ranges (bands) and the acquisition time of the measurements were estimated. In table 4, results also show that oil types present a different wavelength region in which reflectance and oil spill age were correlated. Heating oil, heavy fuel oil and crude oils (apart from Sarir, Blend and REBCO) present high correlation values (0.88, 0.98 and 0.74 respectively) between reflectance values and age. Kerosene presents a relatively low correlation between reflectance values and age, probably due to its aromatic ingredients which evaporates at the first day. As shown in table 4, age of oil spills in hours is given by  $y$  when  $x$  is the average value of reflectance within the corresponding wavelength region for each oil type. Only linear best-fit functions have been used for oil slick age estimation.

Table 4. Estimation of oil slick age

NAME	WAVELENGTH (nm)	VALUE OF CORRELATION	EQUATION	R <sup>2</sup>
HEAVY FUEL OIL	895.35-919.35	0.88	$y = 328.58x - 263.29$	0.88
HEATING OIL	769.00-793.65	0.98	$y = 102.99x - 40.868$	0.98
KEROSENE	576.34-600.38	0.62	$y = 61.398x - 13.141$	0.62
CRUDE OIL	857.66-883.32	0.74	$y = 284.67x - 136.64$	0.85

### 3. CONCLUSIONS

The potentials of hyperspectral data in order to estimate oil slick features such as oil type, the oil slick thickness and the age, have been investigated. Different oil types such as crude oils, heavy fuel oils, marine residual fuel oils and light petroleum products (kerosene and heating oil) were collected for the experiments. Laboratory tests included spectroradiometric measurements of the oil samples at different time intervals and for various oil slick thicknesses. Observations and analysis of oil spectral signatures showed that for near real-time data, the wavelength region around 344.51 nm is the most appropriate for oil type discrimination. At this wavelength region, signature ratios between oil reflectance values and reflectance values of pure water are kept constant, and characteristic for each oil type. Correlation analysis between oil spill reflectance values and oil spill thickness showed that each oil type is highly correlated in a

specific wavelength region. These regions are found within the interval 474 - 917 nm. Correlation between oil spill reflectance values and oil spill age is also high for specific wavelength regions, for each oil type. These regions are found within the interval 576 - 919 nm. The estimated best-fit functions present high R-squared values, and are promising for the reliable estimation of oil slick thickness and weathering state, in case of oil spill maritime events. The results of the laboratory hyperspectral experiments should be evaluated, using remote sensing hyperspectral imagery.

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