Thermal Infrared Remote Sensing of Crude Oil Slicks

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It is important to develop a remote sensing technique for reliable detection of oil slicks for reasons of both oil exploration and environmental protection. Yet, unambiguous detection has proven an elusive goal. This article presents new thermal infrared spectra of oil slicks made from five different crude oil samples with a wide range of API gravities and compositions. After a brief outgassing phase, all oil slick spectra are quite similar and little affected by thickness, extended exposure to air or sunlight, and even by emulsification with seawater (mousse formation). Thus, oil slicks provide a remarkably unvarying spectral signature as remote sensing targets in the thermal infrared compared to other regions of the spectrum. This spectral signature in the 8-14 \( \mu m \) atmospheric window is flat, with an average reflectance of 4%. Seawater, on the other hand, has a spectrum that varies in reflectance with wavelength in the 8-14 \( \mu m \) window from 0.90 to 3.65%. In addition, we show that sea foam displays a reflectance spectrum quite similar to that of seawater in the 8-14 \( \mu m \) region, because the very high absorption coefficient of water in this wavelength region prevents volume scattering in foam bubbles. This results in a relatively uniform spectral background, against which oil slicks can be detected, based on their different spectral signature. Thus, thermal infrared multispectral remote sensing appears to offer a simple and reliable technique for aircraft or satellite detection of oil slicks.

INTRODUCTION

The detection of oil slicks is an important remote sensing objective for both exploration and environmental applications. For exploration, persistent or recurrent oil slicks can point to the presence of undersea oil seeps. For environmental applications, early detection of anthropogenic oil slicks can make possible timely protection of critical habitats and help identify polluters.

Small wonder, then, that repeated efforts have been made to develop remote sensing techniques for oil slick detection. Such techniques have used the entire available electromagnetic spectrum, from UV through microwave wavelengths, but with mixed results. One of the more successful efforts has been in the UV, where oil fluoresces (Maurer and Edgerton, 1976; Camagni et al., 1988), but atmospheric transmission is poor in this region, making satellite observations very...
difficult. Oil slicks have also been identified in the visible and reflected infrared region of the spectrum (Deutsch and Estes, 1980). However, the spectral reflectance properties of different crude oils vary. Our samples, for example, produce slicks that vary in color from pale yellow through brown to black. An additional complication arises in reflectance measurements from the fact that surface roughness changes the reflectance of water, due to the backscatter of sun glint from wave sides oriented at the specular angle, as does the presence of sea foam. As a result, reflectance contrasts between water and oil at any given wavelength in the visible and near-infrared may vary with sea state. Thus, no single processing algorithm is able to identify all oil slicks in the reflective region of the spectrum. In both the thermal infrared and microwave regions of the spectrum, oil has a lower emissivity than water (Buettner and Kern, 1965; Hashimoto et al., 1985), resulting in a brightness temperature contrast that may be used for oil slick detection. However, variations in real kinetic temperature of water can produce false targets, and oil slicks and surrounding water may not be at the same temperature. Finally, the smoothing effect of oil on water has been detected by radar in the microwave region of the spectrum (Estes et al., 1985). However, there are other reasons than the presence of oil for relatively smooth patches of water, and the danger of false targets is again high. Thus, although oil slicks (especially known slicks) have been repeatedly detected using different regions of the spectrum, no single technique has been developed that unambiguously and reliably detects all oil slicks, and current best practice is to use a costly combination of techniques, including airborne radar and a combined IR/UV line scanner for slick detection (Hurford and Tookey, 1990).

We explore here in detail the infrared spectral emissivities of oil and seawater, which have been reported on briefly earlier (Salisbury and D’Aria, 1992), and how this spectral behavior might be used in relatively simple multispectral thermal infrared detection of oil slicks.

**EXPERIMENTAL METHOD**

**Samples**

Sea water was collected off Dana Point, San Juan Capistrano, California. Oil samples used to make slicks on the sea water samples were provided by Chevron Oil Field Research Company, which also provided chemical and physical analyses of the oil samples (Table 1). Slicks of different thicknesses were produced by using a micropipette to place a known volume of oil on a known surface area of water in a petri dish.

**Acquisition of Spectra**

Directional hemispherical reflectance (R) was measured, because directional emissivity (E) can be predicted from such measurements using Kirchhoff's law, stated in its simplest form (without wavelength and directionality subscripts) as $E = 1 - R$ (Nicodemus, 1965). Reflectance spectra were measured at 4 cm$^{-1}$ resolution using a Nicolet System 510 interferometer spectrometer. The Nicolet System 510 can switch the infrared beam from the sample compartment to an external port, through which it exits in collimated form. An integrating sphere, coated inside with a diffusely reflecting gold surface, was attached to the instrument at this port. The sphere is 12.7 cm in diameter and has a 2.5 cm diameter entrance port in the top of the sphere at 10° off the vertical, through which the beam passes to fall on a 2.5 cm diameter sample/reference port in the bottom

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Geographic Location</th>
<th>API Gravity</th>
<th>Sulfur (wt %)</th>
<th>Saturates (wt %)</th>
<th>Aromatics (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35473</td>
<td>Offshore, Louisiana</td>
<td>25.2</td>
<td>0.24</td>
<td>48.3</td>
<td>22.6</td>
</tr>
<tr>
<td>39076</td>
<td>Offshore, California</td>
<td>22.3</td>
<td>2.50</td>
<td>32.3</td>
<td>23.6</td>
</tr>
<tr>
<td>42657</td>
<td>North Sea, Denmark</td>
<td>47.8</td>
<td>0.03</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>34792</td>
<td>North Slope, Alaska</td>
<td>24.4</td>
<td>0.88</td>
<td>29.7</td>
<td>21.7</td>
</tr>
<tr>
<td>15465</td>
<td>L. Maracaibo, Venezuela</td>
<td>31.7</td>
<td>1.11</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
of the sphere. Beam size on the sample in that bottom port is 1.54 cm. A 2.5 cm detector port is placed at an angle of 90° to the principal plane in the side of the sphere, and the liquid-nitrogen-cooled, mercury–cadmium–telluride (MCT) detector chip is baffled to eliminate direct viewing of either the sample or the specular “hot spot” on the sphere wall. A port at the specular angle was filled during the measurements reported below with a gold-coated plug having a surface curved to match the interior curvature of the sphere.

The integrating sphere uses a Labsphere diffuse gold (Infragold) surface as a reference. Sphere performance was carefully calibrated to provide absolute reflectance. Standards traceable to the National Institute of Standards and Technology (NIST) were available from 2.1 μm to 2.5 μm (we used Labsphere certified reflectance standards). There are, however, no NIST reflectance standards at longer wavelengths in the infrared, so we linked the reflectance values determined in the 2.1–2.5 μm region to the 8–14 μm region (and points in between) using fresh, front-surface aluminum- and gold-coated mirrors to calibrate for high reflectance values, and water and a black body cone for the low range. We assumed a flat reflectance of 97% and 98%, respectively, for aluminum and gold mirrors in the 8–14 μm region, and used the optical constants of Downing and Williams (1975) to calculate the reflectance of distilled water. Distilled water is a particularly good standard with which to measure spectrometer performance, because it is widely available and its very low reflectance tests the signal-to-noise capability of the instrument, as well as its linearity of response from high to low range.

To test the accuracy of our measurements, an average of 10, 500-scan, calibrated spectra of distilled water was compared with a spectrum of distilled water calculated from the optical constants of Downing and Williams (1975). This comparison showed a mean deviation of 0.17% (i.e., not 0.17% of the calculated value, but an absolute variation of 0.17% reflectance). All deviations were systematically higher than the calculated values. This systematic deviation can be explained in large part by the 5°C lower temperature of our water sample, which will have raised the reflectance slightly (Pinkley et al., 1977). Thus, we can say that the absolute accuracy of our measurements is considerably better than 1%. When multiple measurements are averaged, as we have done for water, the accuracy appears to be in the 0.10% range. The reproducibility of our spectral measurements was tested by determining the standard deviation of the 10 reflectance measurements of distilled water cited above from their average spectrum. The standard deviation averaged 0.02% over the entire wavelength range 2.1–14 μm, with a lower value (0.01%) in the middle of the wavelength range, where energy and signal-to-noise are high, and a higher value (0.09%) near 14 μm, where energy and detector sensitivity both decline rapidly.

RESULTS AND DISCUSSION

Spectra of Oil Slicks

Spectral Effects of Composition: Spectra of mature (see effects of age below) slicks of five crude oils of very different compositions and physical properties (Table 1) were measured. As shown in Figure 1, spectra of these slicks display relatively little difference throughout the spectral range considered here. The most variance is seen in the 2–2.5 μm reflective region of the spectrum, which is consistent with the difficulty experienced in reliably identifying oil slicks in reflectance. The
major spectral features seen in these spectra are due to the fundamental C–H stretching and bending vibration bands. The nature and origins of such features in infrared reflectance of natural materials is discussed elsewhere (Rowan et al., 1991). We are not concerned with them here, because they fall outside the useable atmospheric windows. However, in brief, the stronger stretching vibrations result in a sharp Christiansen frequency minimum near 3.3 μm and two reflectance peaks near 3.4 μm and 3.5 μm due to surface scattering. The weaker bending vibrations yield similar, but much weaker, features near 6.7 μm. Aside from these fundamental C–H bands, strongly overlapping bands from the wide range of complex hydrocarbons present in crude oils result in a very flat reflectance spectrum. It has been reported once before (Buettner and Kern, 1965) that oil slicks behave generally as gray bodies in the 8–14 μm region. We show here that not only are the spectral curves flat over a much larger wavelength range, but also that they have a similar (within 1%) reflectance level, despite the wide variation of crude oil types represented.

**Spectral Effects of Slick Thickness:** Oil slicks of different thicknesses were made by pipetting larger and larger amounts of oil onto the water surface. Constrained by the sides of the petri dish, this produced progressively thicker slicks. As shown in Figure 2, slick thickness had a negligible effect on spectral reflectance, at least in the 8–14 μm range, the slight variations displayed being consistent with experimental reproducibility of these 500-scan spectra. The thinnest slick in Figure 2 is 0.22 mm. It is difficult to make thinner slicks, even with the low-viscosity oils, that are also continuous across the container. However, slicks as thin as 0.08 mm (assuming uniform thickness across the width of the slick) were achieved by blowing gently on a slick surface to spread it. All slicks of all thicknesses displayed the same spectra as thicker slicks, when allowed to age sufficiently to allow volatile loss (see below).

**Spectral Effects of Slick Age:** A fresh slick releases hydrocarbon volatiles at a high enough rate to form a cloud of vapor above the slick surface, even in the continuously purged spectrometer. As shown in Figure 3, this cloud absorbs very strongly in the region of the C–H stretching fundamentals from 3.2 μm to 3.5 μm, eliminating any trace of the surface scattering peaks near 3.4 μm and 3.5 μm. Two strong vapor absorption bands are also seen near 7.2 μm and 6.8 μm. The different species of hydrocarbons present at the surface during outgassing, compared to those present on the surfaces of aged slicks, evidently accounts for the slight rise in reflectance in the 12 μm region.

A spectrum of the same slick measured after 20 h shows none of the gas absorption or emission
features and is quite flat in the 8–14 μm region (Fig. 3). Such a spectral change does not require 20 h of outgassing for slicks of the thickness studied here. In fact, this change occurs for slicks as much as 3 mm thick in a matter of 10 or 20 min. Obviously, much thicker slicks are possible for large oil spills, and outgassing time for such spills may increase accordingly.

Slicks were left exposed to laboratory air for as long as 21 days, and to sunlight for as long as 20 h, to seek other possible aging effects. The only effect noted for all slicks was a slight (typically <0.3%) rise in overall reflectance. Only the spectrum of sample #42667 showed a larger rise (~0.5%), accompanied by much stronger reflectance peaks near 3.4 μm and 3.5 μm. This behavior appears to be related to formation of a thin skin of brittle, paraffinlike material on the surface of the slick.

**Spectral Effect of Agitation:** Agitation of the water, as in wave action, can emulsify the oil and water to form a “mousse.” Mousses were initially made in the laboratory by whipping an oil/water mixture with a fork until a thick, viscous mass remarkably similar to a chocolate mousse formed. Ultimately, a blender was used to create very viscous samples of mousse. Repeated experiments with the same oil yielded slightly different spectral results. However, the spectra were essentially flat in the 8–14 μm region and varied by no more than 1% from the spectrum of a simple slick of the same oil (Fig. 4).

**Spectra of Water and Foam**

Buettner and Kern (1965) determined that water had a broad-band emissivity of 0.993 in the 8–12 μm region, and subsequent researchers have often rounded this up to 1.0 and assumed a flat spectral response for water throughout the 8–14 μm region. However, Buettner and Kern referenced and illustrated (their Fig. 2) a spectrum of water that was not flat, and which indicated that their measurement of emissivity might be too high. This has been confirmed by subsequent measurements of water spectra (Downing and Williams, 1975), including our own (Salisbury and D’Aria, 1992) (Fig. 5). Seawater and distilled water have slightly different reflectance properties, and water spectra vary slightly in overall reflectance with temperature (Pinkley and Williams, 1976; Pinkley et al., 1977); but spectra of seawater and distilled water near room temperature are virtually indistinguishable at the scale of Figure 5, and so only the spectrum of seawater is shown.

The average emissivity of seawater in the 8–12 μm region calculated \( E = 1 - R \) from the spectrum in Figure 5 is 0.986. In Band 6 (10.4–12.5 μm)
of the Landsat Thematic Mapper, we similarly calculate an emissivity for seawater of 0.989. On the other hand, the average emissivity in TM Band 6 calculated for our aged crude oil slicks is 0.96. A difference of 0.01 in emissivity results in an apparent difference of 0.6°C in temperature in this wavelength region at room temperature, showing why oil slicks and seawater may display brightness temperature contrasts in Thematic Mapper Band 6 data. Unfortunately, real differences in temperature between oil slicks and nearby seawater caused by differing absorption of sunlight may disguise the effects of emissivity differences, making nighttime measurements desirable. Even then, real water temperature differences due to currents may introduce false targets. Thus, the only unambiguous difference between spectra of oil slicks and seawater lies in the different shapes of their spectral curves, usually referred to as their spectral signatures. In the visible, sea foam is a substantial variable affecting the apparent spectral signature of seawater, so we investigated the spectral behavior of sea foam in the infrared.

Foam spectra are difficult to obtain in the laboratory because of the ephemeral nature of foams. Consequently, a small amount of ordinary detergent was added to seawater to reduce its surface tension and increase the lifetime of its foam (considering current ocean pollution, this may not be a completely unrealistic composition). Figure 5 shows that, at least in the 8–14 μm region, the presence of foam does not change the infrared spectrum appreciably, despite greatly different reflectances for foam and seawater in the visible region of the spectrum. This difference in spectral behavior between the visible and infrared occurs because the absorption coefficient of water is relatively low in the visible, allowing volume scattering in foam bubbles and enhanced backscatter compared to a liquid water surface, making foam bright. In the 8–14 μm region, however, the absorption coefficient is so great that negligible volume scattering takes place in the foam bubbles, and the spectrum remains relatively unchanged. The significance of this finding is that the spectral background against which oil slicks must be detected is relatively constant.

CONCLUSIONS

We have shown that the spectral behaviors of oil slicks and seawater in the 8–14 μm atmospheric window are both distinctly different and surprisingly unaffected by variables that might be expected to alter them. If these laboratory results are confirmed by field measurements of actual slicks, thermal infrared multispectral remote sensing appears to offer a simple and unambiguous technique for aircraft or satellite detection of oil slicks. The spectral differences displayed in Figures 1 and 5 are well within the detection range of modern airborne scanners, such as the Thermal Infrared Multispectral Scanner (TIMS) described by Kahle and Goetz (1983), although an additional spectral band would have to be added in the 12.5–13.5 μm region for this system to take advantage of the full range of spectral differences between oil slicks and seawater.

REFERENCES


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