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OAA Technical Memorandum NESS 105



OPTICAL MEASUREMENTS OF CRUDE OIL
SAMPLES UNDER SIMULATED CONDITIONS

Washington, D.C.
October 1979

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OPTICAL MEASUREMENTS OF CRUDE OIL SAMPLES UNDER SIMULATED CONDITIONS

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ABSTRACT. Spectrographic measurements of the solar reflectance from 0.2 to 2.4 μm and radiometric equivalent blackbody temperature measurements from 10.5 to 12.5 μm were made on 10 different types of crude oil under simulated aging conditions of sun, wind, and salt water wave action at the USEPA OHMSETT site in Leonardo, N.J. Four days of exposure produced little change in the reflectance from 0.2 to 2.4 μm , but oil-water temperature differences of up to 18°C were recorded in the 10.5 to 12.5 μm region. Large changes in viscosity were also measured.

1. INTRODUCTION

The spectral signature of crude oil is of interest in evaluating the potential of optical remote sensors for use in observing spills such as those that occurred after the accidents involving the Torrey Canyon, Argo Merchant, and Amoco Cadiz. Such accidents result in the discharge of large quantities of oil into the ocean - 63 million gallons in the case of the Amoco Cadiz. Such a vast amount of oil can cover a large area in a short time, and it would be useful if remote sensors, with their inherent ability to observe large areas in short time periods, could be used to observe the spread of the oil.

Unfortunately, crude oils are normally poor reflectors in the visible and near infrared where reflectance of sunlight can be observed and, since the ocean reflects little sunlight in areas outside its mirror image on the surface of the water, little contrast is observed in the visible or near infrared. The ultraviolet spectral region and polarization measurements (Millard and Arvesen) and laser-induced fluorescence (Fantasia and Ingrao) appear promising, but are restricted by atmospheric interference or signal strength to low altitude measurements. Low altitude, in turn, reduces the advantage of rapid coverage of large areas that remote sensors enjoy.

The possibility of observing oil spills from spacecraft was addressed by Deutsch et al. (1977) and Goldman and Harrath (1975). Deutsch et al. concentrated on oil slicks seen as dark streaks in Landsat imagery. Slicks were associated with known oil spills, but imagery from a U-2 aircraft, used by NASA for ocean color observations, has shown dark streaks on the ocean surface in many cases where no oil spill was known to have occurred (Hovis and Leung 1977). In fact, in the photography from the U-2 at 65,000 feet, dark streaks were seen more often than not.

Goldman and Harrath pointed out many of the problems associated with oil spill detection from satellites, but recognized that satellite data could be useful, "in conjunction with other current methods."

One question that concerned us was the possible change in the spectral character of crude oil with time after it was discharged into the ocean. Deliberate oil spills have, of necessity, been limited to small quantities, so if has not been possible to study the oil as it aged since the oil had dispersed. Few examples of the spectral signatures from large accidental spills are obtainable since spectral measuring devices are not readily available at such spills.

In order to study the spectral signature of aging crude oil under controlled conditions, the USEPA was approached to acquire the use of the OHMSETT (Oil and Hazardous Materials Simulated Environment Test Tank) facility in Leonardo, New Jersey, to conduct the tests. John Farlow and his group from EPA responded enthusiastically and tests were scheduled for August 1978.

2. EXPERIMENTAL PROCEDURE

In order to contain the crude oil samples, wooden cells were designed and built by the USEPA personnel at OHMSETT. These floating cells were open at the top and bottom to allow sunlight and air to reach the samples for evaporation of volatile components and dissolution into the salt water contained in the tank. The water is pumped into the tank from Raritan Bay and filtered. The water in the tank is then clean salt water with only the filterable solids removed.

Ten floating cells were fabricated, each approximately 1.3 x 1.3 meters and with sides projecting approximately 30 cm above and below the water (fig. 1). The insides of the cells were painted a non-reflecting black to minimize reflections from the walls. The cells were positioned by ropes from either side of the tank to keep them centered in the tank and positioned underneath the sensors (fig. 2).

The OHMSETT tank has a movable bridge, spanning the width of the tank, which provides the necessary electrical power to operate sensors, while allowing the instruments to be positioned along the length of the tank.

The sensors used were a Filter Wedge Spectrometer (FWS), a Barnes PRT-5 radiometer, and a closed circuit TV system. The FWS scanned spectrally from 0.4 to 2.4 μm and is of the type described by Hovis, Kley and Strange (1967). It viewed the sample in the vertical direction from a catwalk extended from the bridge. The field of view of the spectrometer covered 0.5 x 0.5 meters at the surface of the oil. The spectral resolution is approximately 1 percent of the wavelength, e.g., $\Delta\lambda = .015 \mu\text{m}$ at 1.5 μm . The Barnes PRT-5, filtered to 10.5 to 12.5 μm , vertically viewed a circular 0.6-meter diameter area of the oil sample.

The closed circuit TV system was aligned with the sensors to view the sample cells in order to determine not only that the sensors viewed the oil surface, but that the field of view was not shadowed by the sides of the cell. In

retrospect, wider cells would have reduced the percentage of the oil shadowed by the vertical sides in the morning and afternoon. The readout for the TV, together with the recording apparatus for the data from the other sensors, was situated in a small shed located on the movable bridge.

In order to prevent reflected sunlight from the bottom of the tank (which was painted a light green) from influencing the measurements of spectral reflectance, a large square plate, painted flat black, was placed underneath the cell whenever the reflected sunlight from the oil was to be measured (fig. 3). For solar reference, another plate, coated with diffuse white paint (a mixture of $\text{MgO-Al}_2\text{O}_3$), was swung into the field of view directly over the sample.

The OHMSETT is equipped with a wave-generating facility that was used to agitate the specimens, simulating ocean wave motion. Since large regular waves caused some oil to splash out of the cells, "harbor chop" equipment was used to produce agitation.

3. SPECIMENS

Ten crude oil samples were acquired for this study. Surprisingly, despite the large number of refineries near the OHMSETT facility, and excellent cooperation by the Sun, Exxon, and Gulf Oil Companies, it was difficult to acquire crude oil in quantities of several gallons because the drawing off of such small quantities at large refineries interrupts routine operations.

The crude oil specimens acquired were as follows:

- | | |
|-------------------------|--------------------------|
| 1. Gabon | 6. North Slope, Alaska |
| 2. Sahara | 7. La Rosa, Mexico |
| 3. Suniland | 8. Lagunillas, Venezuela |
| 4. Arzew, Algeria | 9. Iranian Light |
| 5. Brass River, Algeria | 10. Nigerian |

4. MEASUREMENTS

Spectral and radiometric measurements were begun on August 21, 1978, together with sampling for measurement of viscosity. Viscosity was measured by the EPA personnel in their laboratory adjacent to the tank. Spectral measurements over each cell were conducted once a day on August 21 and August 22, but twice a day on August 23 and August 24, when procedures were better established for moving the bridge and centering the cells. The weather was sunny and warm August 21 to 24. August 25 was overcast and rainy, precluding data acquisition.

Wave agitation was carried out between measurements as shown below:

<u>Date</u>	<u>Minutes</u>	<u>Harbor chop (cm)</u>
August 21	20	28
August 22	20	28
August 23	25	18
August 24	30	18
August 25	20	18

Spectral measurements were made for 4 days and showed little change in the reflective characteristics of the oil with aging. Figures 4 through 13 show the reflected solar energy in units of spectral irradiance for the reference sample and the 10 specimens of crude oil taken on the last day of measurement. Most of the samples exhibited no change in reflective character with age that was detectable with our instrumentation. Note that the scale for the reference sample is given on the left side of the spectral plot and that for the oil, on the right. All the samples appeared to be reasonably gray from $0.4\text{ }\mu\text{m}$ to $1.1\text{ }\mu\text{m}$ (400 to 1100 nanometers) with very low reflectance. The highest reflectance measured was about 1.7% for the Arzew Algerian crude, (fig. 7) at about 530 nanometers. This, of course, is diffuse reflectance in the nadir direction, but that is the reflected component that would be observed by a satellite sensor.

PRT-5 measurements in the 10.5 to $12.5\text{ }\mu\text{m}$ band were made simultaneously with the spectral measurements. The water in the tank stayed at 25 to 26°C during the tests, but each sample of oil was considerably warmer than the water. The observed water temperature and oil temperature, as measured by the PRT-5, are shown together with the spectra on figures 4 through 13. The temperature differences ranged from 10° to 18°C . This is hardly surprising since the dark crude oil samples absorbed the incident sunlight, while the water in the tank was clear and much of the sunlight was transmitted to the bottom and sides of the tank and reflected back out of the tank. In the ocean, only a small fraction of the incident sunlight would be reflected, but absorption would take place over a long path length, depending upon the water clarity, and heating would be distributed over considerable depth, not concentrated at the surface. In the ocean, as in the tank, one would then expect an oil slick to be warmer under sunlit conditions than the surrounding water surface. This indicates that under clear skies and sunlight, the best spectral region for optical remote sensing of oil from satellites would be the thermal infrared.

As mentioned previously, samples of the crude oil were measured daily for viscosity. Figures 14 and 15 show the viscosities measured as a function of time after the oil was placed on the surface of the water. In general, the viscosities increased with time as volatiles evaporated and solubles dissolved except for one case of Algerian crude whose viscosity increased, then dropped sharply. The viscosity of Lagunillas crude dropped after 48 hours, but rose again after 72 hours to reach the highest viscosity of the samples measured.

It was evident that the volatiles were evaporating since, on the first day, the entire area had a strong petroleum odor, but by the fourth day, very little odor could be detected. Samples of the fresh and aged crude were maintained and the change in odor is easily detectable in those samples, so the effect was not one of conditioning of the experimenters' olfactory senses due to exposure.

5. CONCLUSIONS

The reflectance of the crude oil samples tested under simulated aging conditions changed insignificantly with time. The reflected signal levels that would be seen from a satellite viewing sunlit oil on the ocean surface are small, but possibly detectable in the 0.4 to $1.1\text{ }\mu\text{m}$ region. From 1.1 to $2.4\text{ }\mu\text{m}$, the reflected signal levels are so low that there appears to be no

rationale for looking for oil spills in that spectral region.

Crude oil floating on the ocean surface will be extremely difficult to detect when the water is deep and reasonably clean. In cases where the water has higher reflectance, such as an area where there is a large concentration of suspended sediments or organic growth, oil might be detected as a dark patch against a lighter background. This would also apply over shallows where bottom reflectance would provide a bright background.

Searching for oil slicks in glint patterns may be of some value from aircraft where angles of view can be controlled. But in the case of spacecraft, where view angles are dictated by orbital geometry, it is doubtful that practical use could be made of this technique. The Coastal Zone Color Scanner (CZCS) on Nimbus-7 has a tilt mechanism for avoiding glint that could be commanded to look into the glint, but glint would not cover the entire image, only a fraction of the 1600-km swath. It would be rare that an oil spill would be viewed in that fraction of the swath. In any event, as noted earlier U-2 imagery and photos have shown many dark streaks in sun glint that cannot be attributed to any known oil spill.

From our measurements, temperature differences offer the most promise for oil spill detection by optical sensors from satellites, but are limited by the need for clear skies to provide both the opportunity to observe the ocean surface, and sunlight to produce the thermal contrast.

ACKNOWLEDGMENTS

Grateful acknowledgments are made to L. R. Blaine of NASA Goddard for the use of the Filter Wedge Spectrometer, and to C. Jones, R. Levin, P. Bridges, and J. Kapsch of the National Environmental Satellite Service, Satellite Experiment Laboratory, for their helpful efforts.

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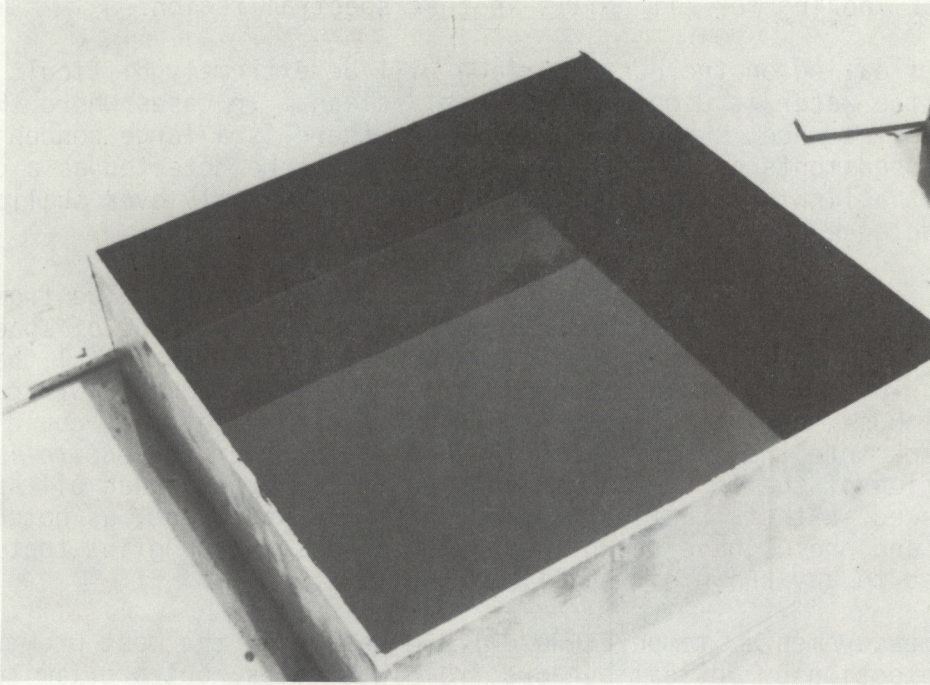


Figure 1.--Floating cell for containing crude oil sample.

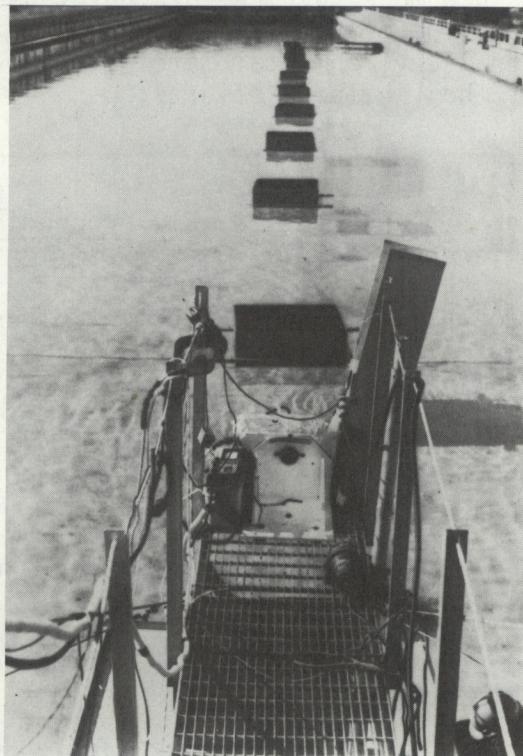


Figure 2.--OHMSETT with sample cells deployed.

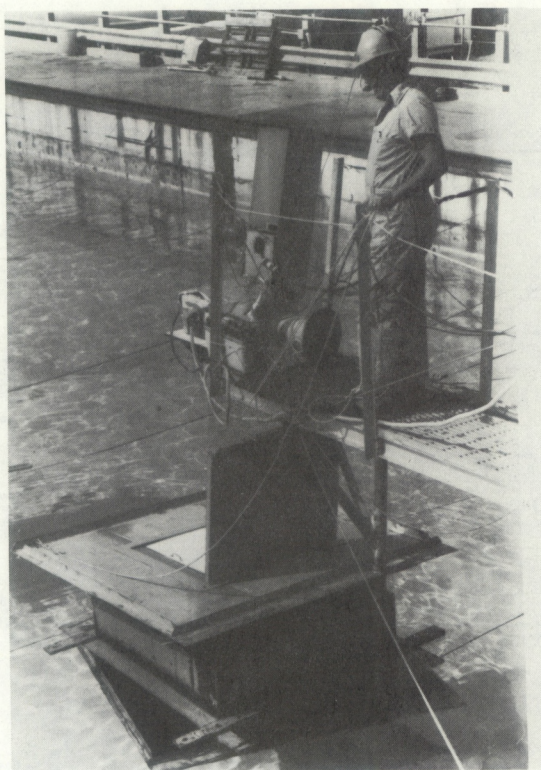


Figure 3.--Catwalk with mounted instruments, solar reflectance reference, and flat black shutter plate.

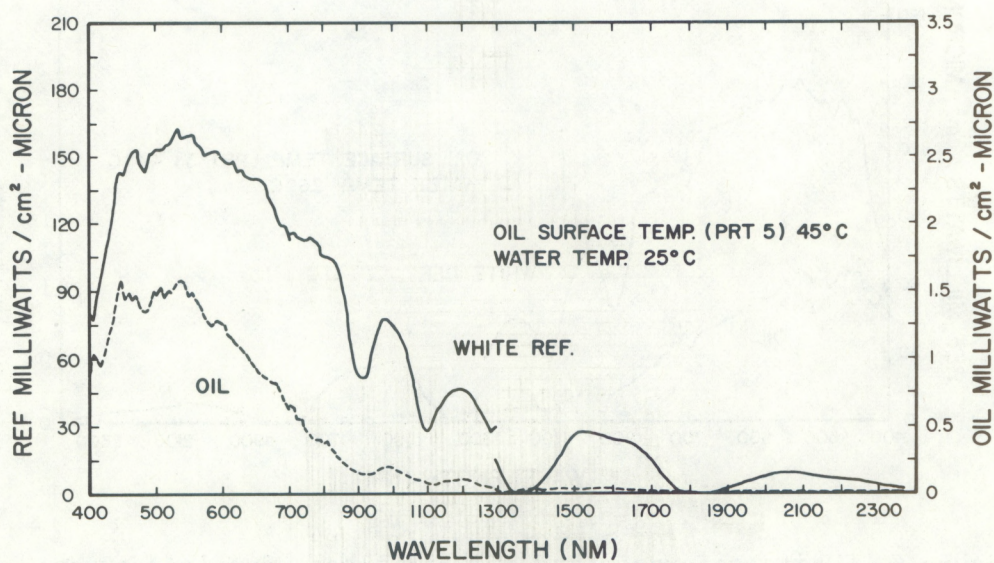


Figure 4.--White reference and oil radiances, Gabon crude; Julian Day 239, 1335 hours.

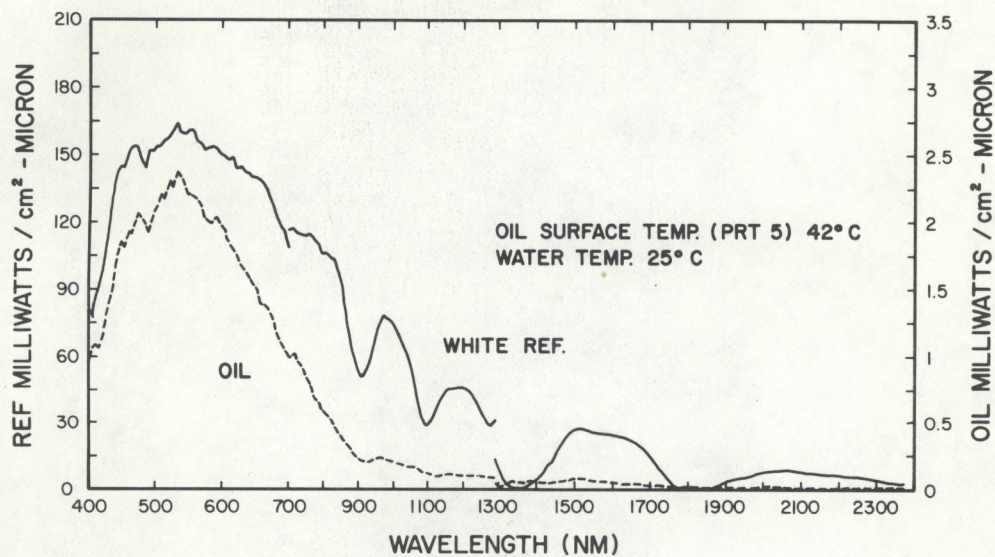


Figure 5.--White reference and oil radiances, Sahara crude;
Julian Day 239, 1349 hours.

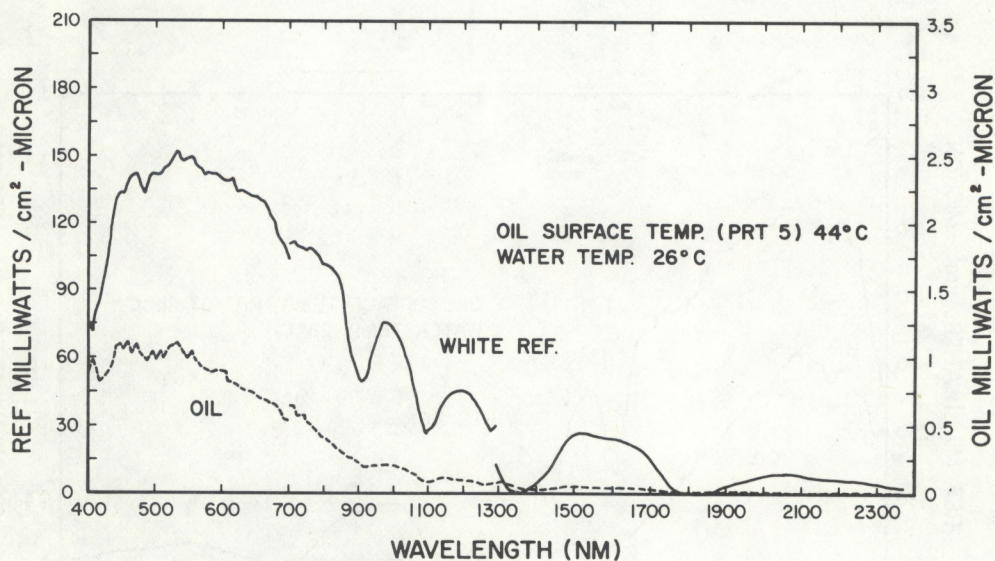


Figure 6.--White reference and oil radiances, Suniland crude;
Julian Day 239, 1402 hours.

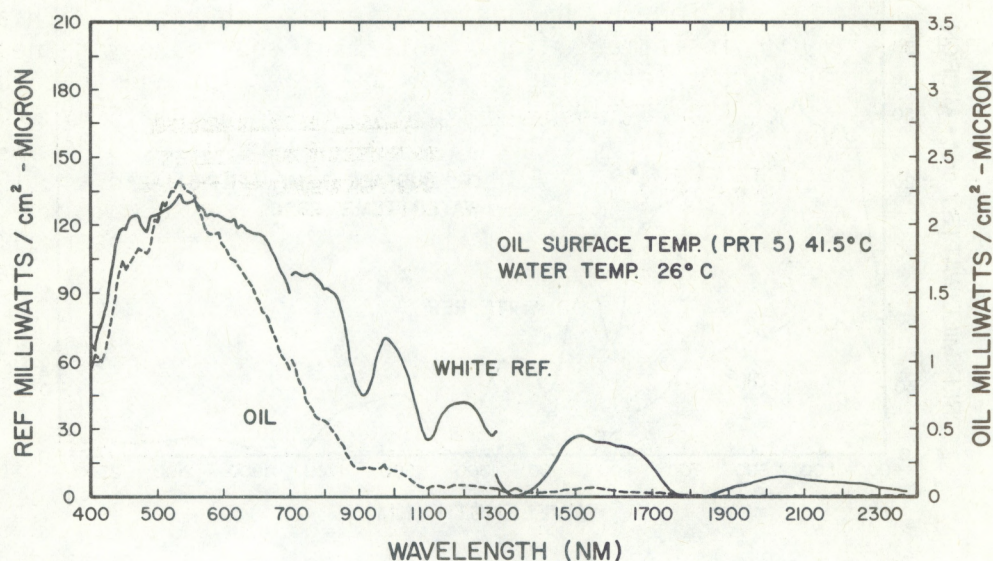


Figure 7.--White reference and oil radiances, Arzew, Algerian crude; Julian Day 239, 1425 hours.

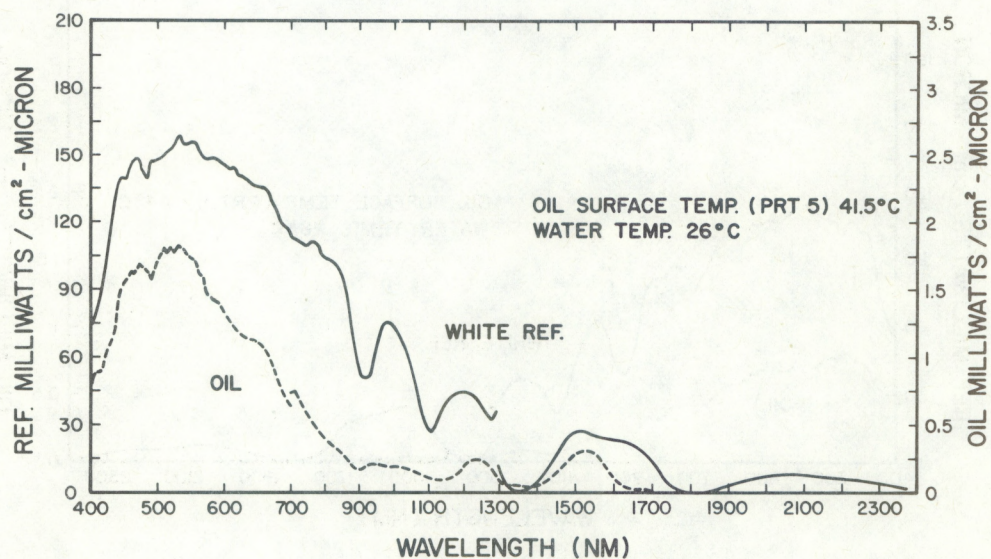


Figure 8.--White reference and oil radiances, Algerian crude; Julian Day 239, 1438 hours.

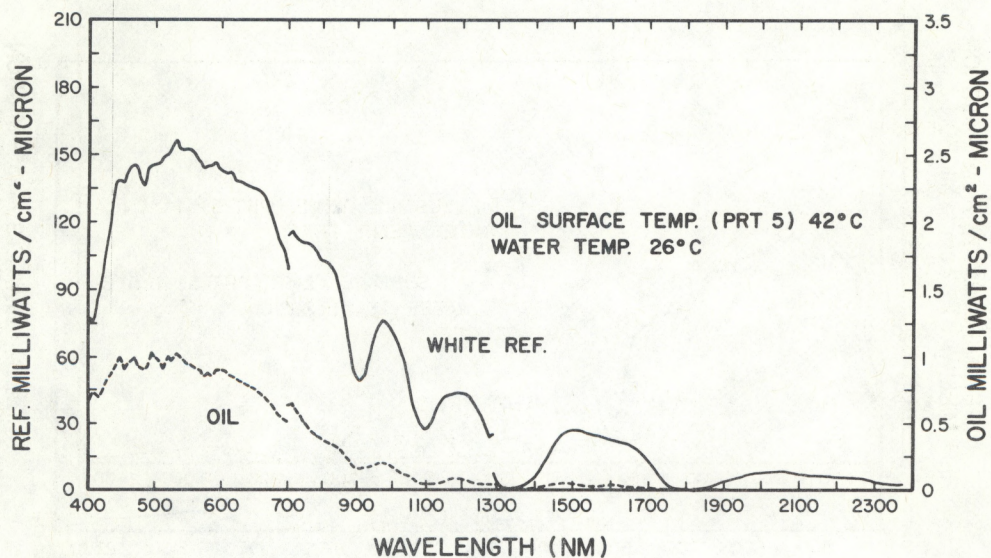


Figure 9.--White reference and oil radiances, Alaskan crude;
Julian Day 239, 1451 hours.

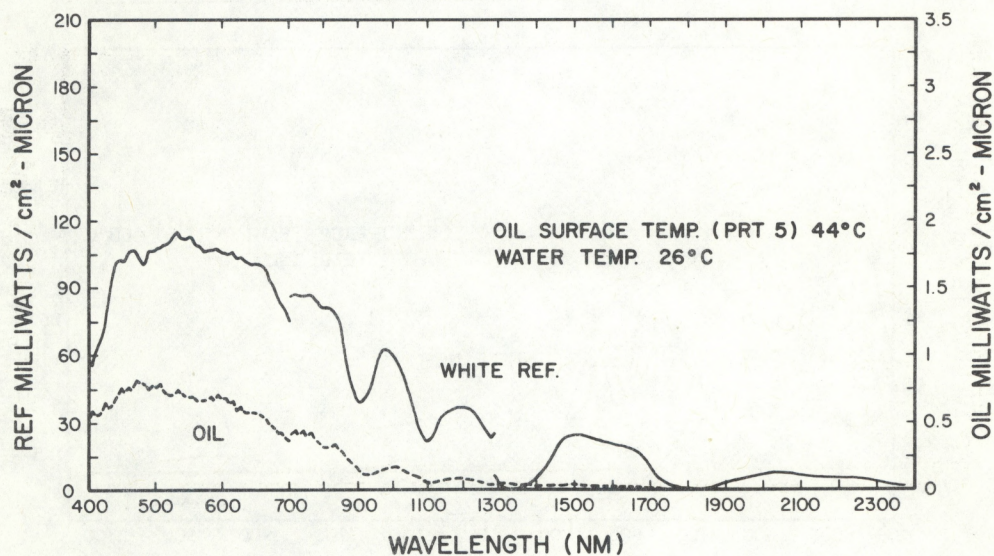


Figure 10.--White reference and oil radiances, Larosa, Mexico, crude;
Julian Day 239, 1512 hours.

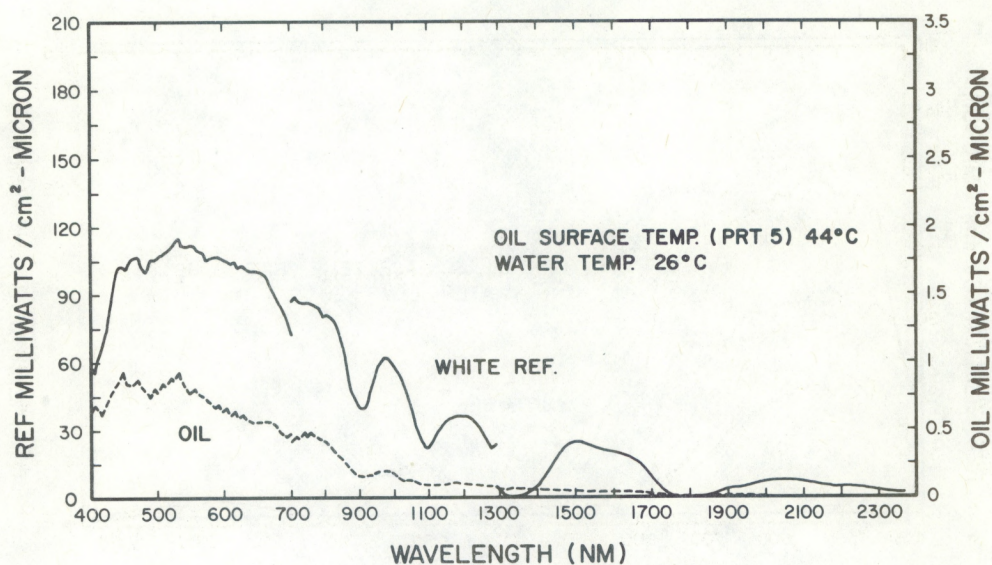


Figure 11.--White reference and oil radiances, Lagunillas, Venezuela crude; Julian Day 239, 1522 hours.

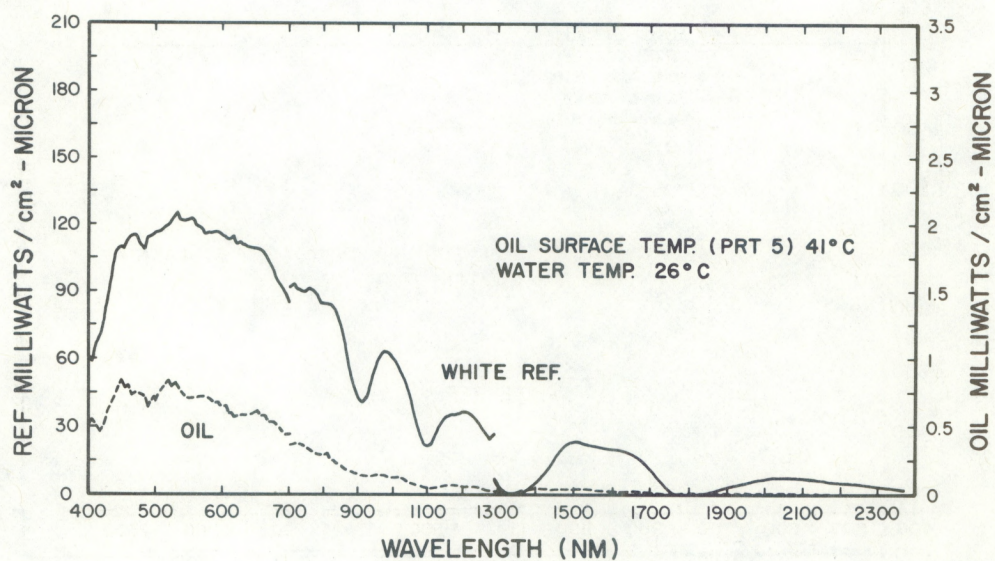


Figure 12.--White reference and oil radiances, Iranian light crude; Julian Day 239, 1535 hours.

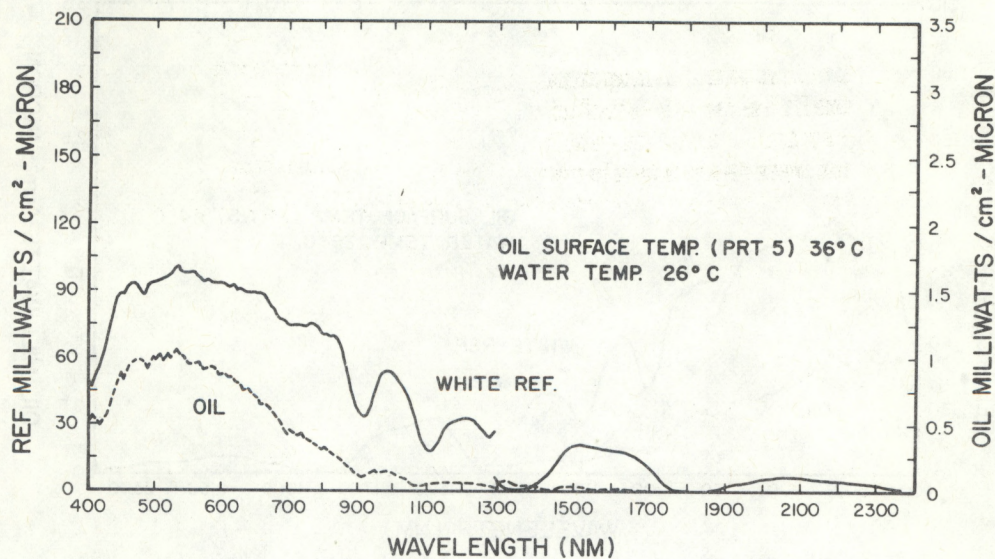


Figure 13.--White reference and oil radiances, Nigerian crude; Julian Day 239, 1550 hours.

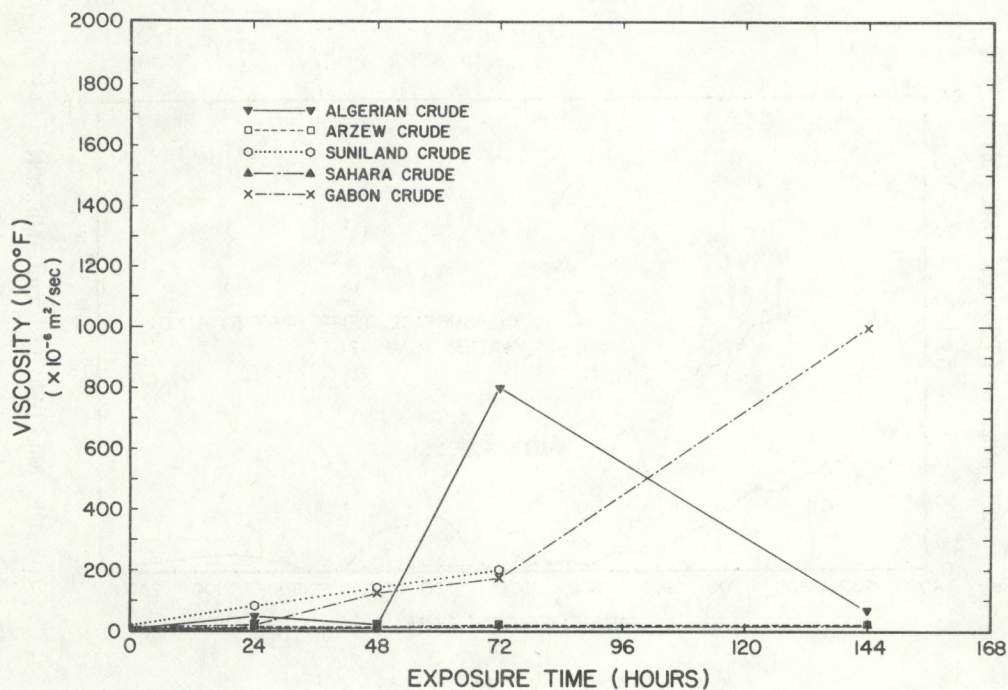


Figure 14.--Viscosity vs. exposure time, five samples.

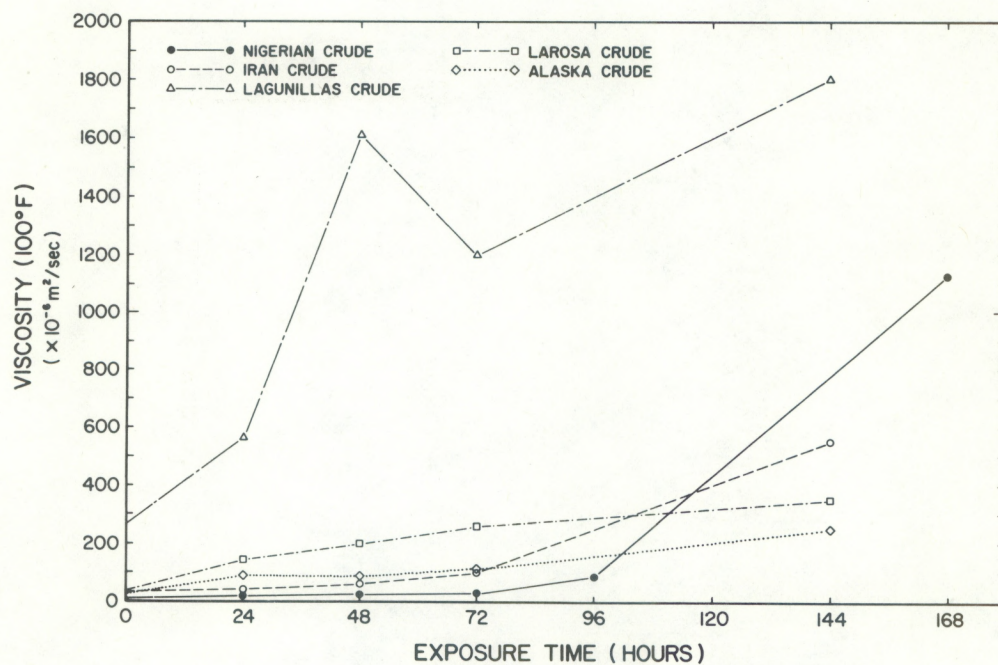


Figure 15.--Viscosity vs. exposure time, five samples.

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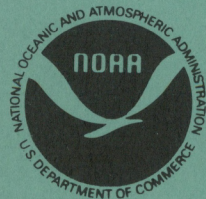
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